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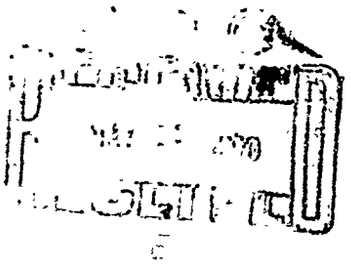

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224

Table of Contents

Report Abstract

Research on simple and complex metal hydrides of lithium, beryllium magnesium, aluminum and boron has been carried out. The work reported herein describes the preparation and structural determination of a number of new hydrides as well as the development of new economic methods for the preparation of known compounds.

The first report describes the preparation of a new class of hydrides, $HMgNR_2$ compounds, and reports that those reactions leading to HMgOR compounds actually produce a mixture of MgH_2 and $MgOR_2$.

The second report describes the preparation of the first complex metal hydrides in which magnesium is the central metal atom. The two compounds prepared thus far are $KMgH_3$ and $NaMg_2H_5$.

The third report describes a most economic route to aminoalanes, $H_nAl(NR_2)_{3-n}$, by the reaction of aluminum, hydrogen and secondary amine. Compounds such as $HAlN(CH_3)_2$ were prepared in essentially quantitative yield.

The fourth report describes a similar route for the preparation of aminoboranes by the reaction of aluminum, hydrogen, phenyl borate and secondary amine. Aminoboranes such as $HBN(C_2H_5)_2$ are produced in ~90% yield.

The fifth report describes a complete evaluation of the reaction of alkali metal hydrides with magnesium halides as a route to active magnesium hydride. Magnesium hydride can be formed in high yield under several sets of conditions.

The sixth report describes the reactions of complex metal hydrides with Grignard reagents to form $RMgAlH_4$ compounds which are precursors to $HMgAlH_4$.

The seventh report describes all attempts thus far to prepare $HMgAlH_4$ and $HMgBH_4$ by two different methods.

The eighth report describes attempts to prepare $Mg(AlH_4)(BH_4)$ and $MMg(AlH_4)_3$ where M = Li and Na.

The ninth report describes a detailed study concerning the preparation of $Be(AlH_4)_2$ from $LiAlH_4$ or $NaAlH_4$ and $BeCl_2$ in diethyl ether or tetrahydrofuran.

The tenth report describes a study of the thermal decomposition of complex metal hydrides by means of the newly acquired DTA-TGA instrumentation.

The eleventh report describes the preparation of a new class of compounds, RMgH.

Two papers have appeared in print during the contract period as a result of work presented initially in the previous report and completed during the present contract. Both of these publications are attached. A third publication also containing work completed during the present contract year is in press and is not included. This work describes the reaction of $LiAlH_4$ with Et_2Mg in diethyl ether solvents.

Concerning the Preparation of Dialkyl(aryl)aminomagnesium Hydrides and Alkoxy(aryloxy)magnesium Hydrides

R. G. Beach and E. C. Ashby

Abstract

Dialkyl(aryl)aminomagnesium hydrides have been synthesized by hydrogenation or $LiAlH_4$ reduction of dialkyl(aryl)aminomagnesium alkyl compounds.

$$R^1MgNR^2_2 + H_2 \rightarrow HMgNR^2_2 + R^1H$$

$R^1 = C_2H_5$, s-C_4H_9

$R^2 = C_2H_5$, i-C_3H_7, n-C_4H_9, C_6H_5

$$4\ R^3MgNR^4_2 + LiAlH_4 \rightarrow 4\ HMgNR^4_2 + LiAlR^3_4$$

$R^3 = C_2H_5$, i-C_3H_7

$= i\text{-}C_3H_7$

The hydrides were characterized by elemental analysis, X-ray powder patterns, infrared, and thermal analysis. Infrared bands in the 1500-1600 cm^{-1} and 650-700 cm^{-1} regions are assigned to Mg-H stretching and bending modes respectively by comparison with the corresponding deuterated compounds. A Hofmann type elimination is proposed to explain the thermal decomposition of

the hydrides. Alkoxy(aryloxy)magnesium hydrides were shown to be unstable and disproportionate to MgH_2 and $(RO)_2Mg$ (R = CH_3, i-C_3H_7, t-C_4H_9, C_6H_5).

Introduction

Compounds of the type $H_nAl(OR)_{3-n}$,[1] $H_nAl(NR_2)_{3-n}$,[2] $HBeNR_2$ and $HBeOR$[3] are known. Bauer[4] reported the formation of $HMgOC_2H_5$ by C_2H_5MgH cleavage of $(C_2H_5)_2O$, but did not give any evidence that the compound was not a mixture of MgH_2 and $(C_2H_5O)_2Mg$. Coates[3] briefly reported a soluble aminomagnesium hydride when MgH_2 was allowed to react with trimethylethylenediamine in toluene.

Preparation of HMgOR and $HMgNR_2$ compounds was undertaken in order to characterize this class of compounds, and to determine their usefulness as stereospecific reducing agents.

(1) H. Nöth and H. Suchy, Z. Anorg. Chem., 358, 44 (1968).

(2) E. Wiberg and A. May, Z. Naturforsch., 10b, 234 (1955); J. K. Ruff and M. F. Hawthorne, J. Am. Chem. Soc. 82, 2141 (1960).

(3) N. A. Bell and G. E. Coates, J. Chem. Soc. (A), 823 (1968).

(4) R. Bauer, Z. Naturforsch., 17b, 201 (1962).

Experimental

Apparatus. - Reactions were performed under nitrogen at the bench. Filtrations and other manipulations were done in a glove box equipped with a recirculating system using manganese oxide columns to remove oxygen and dry ice-acetone traps to remove solvent.[5]

(5) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, 1969.

Infrared spectra were obtained on a Perkin Elmer 621 Spectrophotometer. Solution spectra were obtained in a cell with KBr windows and solid spectra were obtained as nujol mulls between CsI plates. X-ray powder data were obtained on a Philips Norelco X-ray unit using a 114.6 mm camera with nickel filtered CuKα radiation. Samples were sealed in 0.5 mm capillaries and exposed to X-rays for 6 hours. D-spacings were read on a precalibrated scale equipped with a viewing apparatus. Intensities were estimated visually. A 300 ml Magne-Drive autoclave (Autoclave Engineers, Inc.) was used for high pressure hydrogenation. DTA-TGA data were obtained simultaneously on a Mettler Thermoanalyzer 2. Platinum crucibles were used to hold the samples and alumina was used as a reference material. An atmosphere of argon was maintained during decomposition.

Analytical. - Gas analyses were done by hydrolyzing samples with hydrochloric acid on a standard vacuum line equipped with a Toepler pump.[5] Magnesium and aluminum were determined by EDTA titration.

Materials. - Methanol (Fisher Scientific reagent grade) was distilled after treating with magnesium metal. t-Butanol (Fisher Scientific reagent grade) was fractionally crystallized under nitrogen. Isopropanol (Fisher Scientific) was distilled after drying over Molecular Sieve 4A. Phenol (Mallinckrodt Analytical reagent grade) was distilled at reduced pressure. Diethylamine, diisopropylamine, and di-n-butylamine (Eastman Organic Chemicals) were dried over Molecular Sieve 4A and distilled prior to use. Diphenylamine (Eastman Organic Chemical) was used without further purification.

Solvents were distilled immediately before use from lithium aluminum hydride or sodium aluminum hydride depending on the boiling point of the solvent.

A solution of lithium aluminum hydride (Ventron, Metal Hydride Division) was prepared by stirring a diethyl ether slurry overnight and filtering through dried Celite Analytical Grade Filter Aid (John-Mansville). The solution was standardized by aluminum analysis. In a similar manner a solution of lithium aluminum deuteride (Metal Hydrides Incorporated) was prepared. Sodium hydride, 57% in mineral oil, was obtained from Alfa Inorganics.

Diisopropylmagnesium and diethylmagnesium were prepared by the dioxane precipitation method.[6] Di-s-butylmagnesium was prepared from active $MgCl_2$ and s-butyllithium in benzene.[7] Magnesium hydride was prepared from $LiAlH_4$ and diethylmagnesium in diethyl ether.[8]

(6) G. O. Johnson and A. Adkins, J. Am. Chem. Soc., 54, 1943 (1932). W. Strohmeier and F. Seifert, Chem. Ber. 94, 2356 (1961).

(7) C. W. Kamienski and J. F. Eastham, J. Org. Chem., 34, 1116 (1969).

(8) G. D. Barbaras, C. Dillard, A. E. Finholt, T. Warlik, K. E. Wilzbach, and H. I. Schlesinger, J. Am. Chem. Soc., 73, 4585 (1951). E. C. Ashby and R. G. Beach, in press.

Anal. Calcd for MgH_2: Mg, 92.3; H, 7.65. Found: Mg, 72.9; H, 6.26; Al, 0; $(C_2H_5)_2O$, 20.8 by difference. The ratio of Mg:H is 1.00:2.07.

Ethylmagnesium t-butoxide (C_2H_5MgOt-C_4H_9) and isopropylmagnesium t-butoxide (i-C_3H_7MgOt-C_4H_9) were prepared by adding an equivalent amount of t-butanol to the appropriate dialkylmagnesium in diethyl ether.[9] The diethyl ether solvent

(9) G. E. Coates, J. A. Heslop, M. E. Redwood, and D. Ridley, J. Chem. Soc. (A), 1118 (1968).

was removed at reduced pressure and benzene solutions prepared.

Diisopropylaminoethylmagnesium ($(i\text{-}C_3H_7)_2NMgC_2H_5$) and di-n-butylaminoethylmagnesium ($(n\text{-}C_4H_9)_2NMgC_2H_5$) were prepared by adding an equivalent amount of the appropriate secondary amine to $(C_2H_5)_2Mg$ in diethyl ether.[10] The diethyl ether

(10) G. E. Coates and D. Ridley, J. Chem. Soc. (A), 56 (1967).

solvent was evaporated and benzene solutions prepared.

$s\text{-}C_4H_9MgN(i\text{-}C_3H_7)_2$, $s\text{-}C_4H_9MgN(n\text{-}C_4H_9)_2$, $s\text{-}C_4H_9MgN(C_6H_5)_2$, and $s\text{-}C_4H_9MgN(C_2H_5)_2$ were prepared by adding an equivalent amount of the appropriate secondary amine to di-s-butylmagnesium in benzene.

Di-n-butylaminomagnesium chloride ($(n\text{-}C_4H_9)_2NMgCl$) was prepared from $i\text{-}C_3H_7MgCl$ and an equivalent amount of $(n\text{-}C_4H_9)_2NH$ in diethyl ether.

Preparation of R_2NMgH ($R = C_2H_5$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, C_6H_5) -

1) Hydrogenation of dialkyl(aryl)aminomagnesium compounds. - Dialkyl(aryl)aminomagnesium alkyl solutions (0.2-0.7 M) in benzene (100 ml) were hydrogenated overnight at 3000 psig. The temperature of hydrogenation depended on the particular alkyl group: 50-70° for the ethyl group and 25° for the s-butyl group. Analytical and spectroscopic data of the precipitates are given in Table 1. Hydrogenation was complete in the reactions performed at 50-70°. At 25° some starting compound was generally found in the filtrate.

2) Reaction of dialkylaminoalkylmagnesium with $LiAlH_4$ and $LiAlD_4$. -

a) $C_2H_5MgN(i\text{-}C_3H_7)_2$ - To a diethyl ether solution of $C_2H_5MgN(i\text{-}C_3H_7)_2$ (38 mmole), $LiAlH_4$ (9.5 mmole) in diethyl ether was added slowly from an addition

funnel. An immediate precipitate formed. Analysis of the precipitate is given in Table 1. The yield of $HMgN(i\text{-}C_3H_7)_2$ is quantitative. In a similar manner $DMgN(i\text{-}C_3H_7)_2$ was prepared.

b) $C_2H_5MgN(n\text{-}C_4H_9)_2$ - To a diethyl ether solution of $C_2H_5MgN(n\text{-}C_4H_9)_2$ (28 mmole), $LiAlH_4$ (7.0 mmole) in diethyl ether was added. No precipitate formed. Evaporating the diethyl ether and adding benzene or hexane was not effective in separation of the products.

3) Reactions of MgH_2 and Trimethylethylenediamine. - A slurry of MgH_2 (10 mmole) in benzene (50 ml) was reacted with an equivalent amount of trimethylethylenediamine for several days under refluxing conditions. The reaction still contained a solid which was isolated by filtration. The solid was identified as MgH_2 by its infrared spectrum. 4.1 mmoles of MgH_2 was recovered. The filtrate showed no hydridic activity. Evaporation of benzene from the filtrate resulted in a brown oily resin.

4) Reaction of $(n\text{-}C_4H_9)_2NMgCl$ with NaH. - A diethyl ether solution of $(n\text{-}C_4H_9)_2NMgCl$ (70 mmoles) was stirred at room temperature for 3 days with excess NaH. After filtration analysis of the filtrate gave a ratio Mg:H:N as 1.0:1.9:0.912.

5) Reaction of $(i\text{-}C_3H_7)_2NH$ and $(n\text{-}C_4H_9)_2NH$ with MgH_2. - A slurry of MgH_2 (7 mmole) and an equivalent amount of $(i\text{-}C_3H_7)_2NH$ in benzene (-- ml) was reacted for 2 days under refluxing conditions. The solid was isolated by filtration. Infrared spectrum (nujol mull) showed only MgH_2 bands. The filtrate contained no magnesium. In a similar experiment with $(n\text{-}C_4H_9)_2NH$ and MgH_2, the same results were obtained.

A slurry of MgH_2 (10.9 mmole) and an equivalent amount of $(n\text{-}C_4H_9)_2NH$ in benzene (100 ml) was reacted at 200° overnight in the autoclave. The precipitate

was isolated.

Anal: Mg, 45.4; H, 1.82. The infrared spectrum showed Mg-H bands, and X-ray powder lines were those of MgH_2. The filtrate contained no magnesium. In a similar experiment with $(i\text{-}C_3H_7)_2NH$, the same results were obtained.

Preparation of Bis-dialkylaminomagnesium Compounds -

1) $[(C_2H_5)_2N]_2Mg$ - To a diethyl ether solution of $(i\text{-}C_3H_7)_2Mg$ (14.7 mmole), $(C_2H_5)_2NH$ (29.4 mmole) was slowly added at room temperature. An immediate precipitate formed. Analysis of the precipitate is given in Table 1.

2) $[(n\text{-}C_4H_9)_2N]_2Mg$ - In the same manner as above $(n\text{-}C_4H_9)_2NH$ was added to $(i\text{-}C_3H_7)_2Mg$ in diethyl ether. No precipitate formed. After stirring several hours, the diethyl ether was evaporated at reduced pressure. Analysis of the solid is given in Table 1.

3) $[(i\text{-}C_3H_7)_2N)_2Mg$ - In the same manner as above the $(i\text{-}C_3H_7)_2NH$ was added to $(i\text{-}C_3H_7)_2Mg$ in diethyl ether. No precipitate formed. After refluxing several hours the solvent was removed under vacuum.

Anal. Calc. for $[(i\text{-}C_3H_7)_2N]_2Mg$: Mg, 10.82; Calc. for $i\text{-}C_3H_7MgN(i\text{-}C_3H_7)_2$ Mg, 14.51; Found: Mg, 14.37. Infrared spectrum showed a small amount of unreacted amine (1625 cm^{-1}) still remained in the product.

Table 1 - Dialkyl(aryl)aminomagnesium hydrides: Analytical, Infrared and X-ray Powder Data.

Compound	Analytical Calcd.	Analytical Found	Infrared Bands 200...4.0 cm^{-1}	X-ray Powder Data
[a] $HMgN(i\text{-}C_3H_7)_2$	H, 0.803 Mg, 19.37	H, 0.619 Mg, 17.76	1500(Sh), 1335W, 1315W, 1170W, 1050S 1120M, 975S, 935W, 900M, 825W, 810W, 780W, 725S, 690S, 650S, 570M, 535W, 430W	9.5S 5.25S 4.20VVW
[h] $HMgN(i\text{-}C_3H_7)_2$		H, 0.819 Mg, 19.56	1500(Sh), 1330W, 1315W, 1255W, 1170W, 1150S, 1120M, 975S, 935W, 900M, 825W, 810W, 775M, 725S, 690S, 650S, 570S, 545W, 420W	9.5S 5.20S 4.00VW
[i] $DMgN(i\text{-}C_3H_7)_2$		D, 0.719 Mg, 20.17	1330W, 1315W, 1255W, 1170W, 1050S, 1120M, 1050S(B), 975S, 935W, 900M, 825W, 810W, 775W, 715W, 570S, 525S, 465S	———
[b] $HMgN(i\text{-}C_3H_7)_2$		H, 1.45 Mg, 26.90	1590S, 1345W, 1320W, 1170W, 1150S, 1110S, 1090W, 1025W, 975S, 945M, 890S, 820W, 655S, 580S, 425S	11.5S, 5.50S, 4.00M, 3.55W, 2.80VW, 2.15VVW
[c] $HMgN(n\text{-}C_4H_9)_2$	H, 0.656 Mg, 15.83	H, 0.947 Mg, 18.42	1600S(B), 1260W, 1230W, 1215W, 1155M, 1130M, 1105S, 1075S, 1055M, 1010M, 995W, 945M, 915M, 885M, 715S, 675S, 565S, 400S.	12.5S, 4.65S 4.30M, 2.85W
[d] $HMgN(n\text{-}C_4H_9)_2$		H, 0.727 Mg, 16.91	1550S(B), 1300W, 1255W, 1150W, 1130M, 1105M, 1075S, 1010M, 955W, 855M, 790M, 715S, 650M, 570S, 400W	15.0VS 4.40M
[e] $HMgN(C_2H_5)_2$	H, 1.034 Mg, 24.98	H, 0.752 Mg, 20.74	1520S(B), 1295W, 1165M, 1130S, 1095M, 1030W, 1015W, 990M, 845M, 775W, 720S, 670S, 570S, 530S, 440M	14.0S, 4.50VW
[f] $HMgN(C_6H_5)_2$	H, 0.521 Mg, 12.25	H, 0.383 Mg, 10.87	1580S, 1460S, 1370M, 1360Sh, 1330W, 1295M, 1235S, 1215Sh, 1170S, 1070W, 1020M, 870S, 800M, 740S, 680S, 495S, 435W	12.0S, 9.0W, 7.0W, 6.10W, 5.00M, 3.95S, 3.50W, 2.75W, 2.06M, 1.80VW

Table 1 (continued)

Compound	Analytical Calcd.	Analytical Found	Infrared Bands 2000-400 cm^{-1}	X-ray Powder Data
[g]$HMgN(CH_3)CH_2CH_2N(CH_3)_2$	H, 0.797 Mg, 19.92	H, 1.05 Mg, 21.92	1370M, 1340S, 1280M, 1245W, 1190W, 1165M, 1145S, 1105S, 1030S, 940S, 845S, 795S, 670W, 575M, 400S	9.7S, 8.0S, 5.50M, 4.70S, 4.00W, 2.58VW, 2.40W
[j]$[(C_2H_5)_2N]_2Mg$	Mg, 14.42	Mg, 14.10	1255M, 1200W, 1165M, 1255S, 1095M, 1030M, 990M, 915W, 880W, 870W, 845M, 785S, 715M, 670W, 540S, 435M	———
[k]$[(n\text{-}C_4H_9)_2N]_2Mg$	Mg, 8.66	Mg, 8.21	1300W, 1255W, 1215W, 1155M, 1130S, 1115S, 1070S, 1010S, 960W, 885S, 795W, 730M, 580S, 505S	———

[a]Hydrogenation of—$s\text{-}C_4H_9MgN(n\text{-}C_4H_9)_2$ at 25°, [b]$C_2H_5MgN(i\text{-}C_3H_7)_2$ at 70°, [c]$C_2H_5MgN(n\text{-}C_4H_9)_2$ at 50°, [d]$s\text{-}C_4H_9MgN(n\text{-}C_4H_9)_2$ at 25°, [e]$s\text{-}C_4H_9MgN(C_2H_5)_2$ at 25°, [f]$s\text{-}C_4H_9MgN(C_6H_5)_2$ at 25°, [g]$C_2H_5MgN(CH_3)CH_2CH_2N(CH_3)_2$ at 110°, [h]Reaction of—$C_2H_5MgN(i\text{-}C_3H_7)_2$ with $LiAlH_4$, [i]$i\text{-}C_3H_7MgN(i\text{-}C_3H_7)_2$ with $LiAlD_4$, [j]$(C_2H_5)_2NH$ with $(i\text{-}C_3H_7)_2Mg$, and [k]$(n\text{-}C_4H_9)_2NH$ with $(n\text{-}C_3H_7)_2Mg$.

Attempted Preparation of ROMgH -

1) Reaction of MgH_2 and ROH (R = CH_3, i-C_3H_7, t-C_4H_9, C_6H_5) - In a typical case CH_3OH (6.00 mmole) was added to a slurry of MgH_2 (6.00 mmole) in benzene (50 ml). The mixture was stirred overnight under refluxing conditions. The solid was isolated by filtration and dried in vacuo at room temperature. The reaction was repeated with the other alcohols in benzene and tetrahydrofuran (THF). Analytical and X-ray powder data are given in Table 2. In all cases the filtrates contained no magnesium.

2) Hydrogenation of $C_2H_5MgOt\text{-}C_4H_9$ - A 0.5M benzene solution of $C_2H_5MgOt\text{-}C_4H_9$ (50 mmole) was hydrogenated at 110° and 3000 psig in the autoclave overnight. The precipitate was isolated as above. Analytical and X-ray powder data are given in Table 2. The filtrate contained 10 mmoles of magnesium. The ratio of $Mg:H:C_2H_5$ in the filtrate was 1.00:0.0:0.88.

3) Hydrogenation of i-$C_3H_7MgOt\text{-}C_4H_9$ - A 0.3M benzene solution of i-$C_3H_7MgOt\text{-}C_4H_9$ (30 mmole) was hydrogenated at room temperature and 3000 psig overnight. No reaction occurred. The hydrogenation was repeated at 50°C and 3000 psig overnight. The precipitate was isolated as above. Analytical and X-ray powder data are given in Table 2. The filtrate contained 1.0 mmoles of magnesium and no hydridic hydrogen.

Preparation of $(RO)_2Mg$ (R = CH_3, i-C_3H_7, t-C_4H_9, C_6H_5) - In a typical case CH_3OH (8.00 mmole) was added to a slurry of MgH_2 (4.00 mmole) in benzene. After refluxing overnight the solid was isolated by filtration. The reaction was repeated with the other alcohols in benzene and THF. Analytical and X-ray powder data are given in Table 2. In all cases the filtrates contained no magnesium.

Table 2: Analytical and X-ray Powder Data of "ROMgH" Compounds

Compound	Solvent	Mg:H Ratio	X-ray Powder Data
MgH_2	diethyl ether	1:2.07	3.19S, 2.50S, 2.25W, 1.67S
"CH_3OMgH"	benzene	1:1.17	11.0VS, 3.20M, 2.50M, 2.25W, 1.66W
"CH_3OMgH"	THF[a]	1:1.10	11.0VS, 3.20M, 2.50M, 2.25W, 1.68W
$(CH_3O)_2Mg$	benzene	1:0.0	11.0VS
"$i\text{-}C_3H_7OMgH$"	benzene	1:1.02	8.75S, 4.30M, 3.25W, 2.50W, 2.25VW, 1.66W
"$i\text{-}C_3H_7OMgH$"	THF	1:0.78	8.75S, 4.30M, 3.25W, 2.50W, 2.25VW, 1.68VW
$(i\text{-}C_3H_7O)_2Mg$	benzene	1:0.0	8.8S, 4.30M
"$t\text{-}C_4H_9OMgH$"	benzene	1:0.80	9.0S, 8.0M, 4.50M, 4.30M, 4.00VW, 3.45W. 3.25VW, 3.10VW, 2.50VW, 1.68VW
"$t\text{-}C_4H_9OMgH$"	THF	1:0.94	9.0S, 8.0M, 4.50M, 4.30M, 4.00W, 3.45W, 3.25VW, 3.05W, 2.50W, 2.25VW, 1.67W
[b]"$t\text{-}C_4H_9OMgH$"	benzene	1:0.80	9.2S, 8.5M, 4.50M, 4.30M, 3.50W, 3.20M, 2.50M, 2.25W, 1.67W
[c]"$t\text{-}C_4H_9OMgH$"	benzene	1:0.60	8.8S, 7.9M, 4.45M, 4.20W, 4.00VW, 3.45M, 3.25W, 3.05W
$(t\text{-}C_4H_9O)_2Mg$	benzene	1:0.0	9.0S, 8.0S, 4.50M, 4.30M, 4.00W, 3.50M, 3.05W
"C_6H_5OMgH"	benzene	1:0.99	10.5S, 8.5M, 5.05M, 4.60VW, 4.25S, 3.25S, 2.50W, 2.25VW, 1.68W
$(C_6H_5O)_2Mg$	benzene	1:0.0	10.5S, 8.5W, 5.10M, 4.60W, 4.25S, 3.25M
"C_6H_5OMgH"	THF	1:1.05	10.5S, 8.25M, 6.90W, 5.90VW, 4.85W, 4.70W, 4.48M, 4.35M, 4.15M, 3.90M, 3.75M, 3.55W, 3.45M, 3.30W, 3.20W, 3.08VW, 3.02VW, 3.00VW, 2.50W, 2.40W, 2.25VW, 1.87VW, 1.68VW

Table 2 (continued)

Compound	Solvent	Mg:H Ratio	X-ray Powder Data
$(C_6H_5O)_2Mg$	THF	1:0.0	10.5S, 8.25S, 6.95M, 5.95W, 5.15W, 5.40W, 5.15W, 4.50S, 4.35S, 4.15M, 3.90S, 3.80S, 3.65W, 3.45M, 3.30W, 3.20W, 3.00W, 2.90W, 2.80W, 2.70W, 2.40W, 2.25W, 1.86W

[a]THF - tetrahydrofuran

[b]Hydrogenation of $C_2H_5MgOt\text{-}C_4H_9$ at 110° and 3000 psig.

[c]Hydrogenation of $iC_3H_7MgOt\text{-}C_4H_9$ at 50° and 3000 psig.

Results and Discussion

Diisopropylaminomagnesium hydride [$(i\text{-}C_3H_7)_2NMgH$] (I) was synthesized by the hydrogenation of $s\text{-}C_4H_9MgN(i\text{-}C_3H_7)_2$ at 25° and 3000 psig. The filtrate contained 25% of the starting compound but no hydridic hydrogen. (I) had a

$$s\text{-}C_4H_9MgN(i\text{-}C_3H_7)_2 \xrightarrow{H_2} \underset{(I)}{HMgN(i\text{-}C_3H_7)_2} + C_4H_{10} \qquad (1)$$

Mg:H ratio of 1.00:0.84, and a unique X-ray powder pattern which contained no MgH_2 lines (Table 1). The infrared spectrum (nujol mull) of (I) had a broad band at 1500 cm^{-1} appearing as a shoulder on the nujol band at 1455 cm^{-1}. The assignment of this band is discussed below. (I) is insoluble in benzene and diethyl ether, but is soluble in THF to the extent of 0.021 m/l. The molar ratio of Mg:H in the THF solution was 1.00:0.98.

(I) was also prepared by adding a diethyl ether solution of $LiAlH_4$ to an ether solution of $C_2H_5MgN(i\text{-}C_3H_7)_2$.

$$LiAlH_4 + 4\ C_2H_5MgN(i\text{-}C_3H_7)_2 \rightarrow 4\ HMgN(i\text{-}C_3H_7)_2 + LiAl(C_2H_5)_4 \qquad (2)$$

An immediate precipitate formed which could be completely desolvated *in vacuo* at room temperature. The X-ray powder pattern and infrared spectrum (Table 1) were the same as (I) prepared by hydrogenation.

In order to assign the infrared bands $(i\text{-}C_3H_7)_2NMgD$ (II) was prepared from $LiAlD_4$. The infrared spectrum of (II) revealed that the bands present in (I) at 1500, 690, and 650 cm^{-1} were absent in (II) and that the broad bands present at approximately 1050 and 470 cm^{-1} were as predicted for the isotopic shift of

Mg-H to Mg-D. The bands at 690 and 650 cm^{-1} are in the region expected for metal-hydrogen bending modes. The band at 1500 cm^{-1} is probably a terminal Mg-H stretching band. A Mg-H stretching frequency of 1497 cm^{-1} has been calculated from the vapor phase electronic emission spectra of MgH.[11]

(11) M. A. Khan, Proc. Phys. Soc., 80, 523 (1962).

Bridging metal-hydrogen absorption bands occur at lower energy than terminal metal-hydrogen. Absorption centers around 1160 cm^{-1} in MgH_2, which has a rutile structure with magnesium 6-coordinate and hydrogen 3-coordinate.[12]

(12) W. H. Zachariasen, C. E. Holley, Jr., and J. F. Stamper, Jr., Acta Cryst., 16, 352 (1963).

In a similar case, terminal Be-H occurring in $Be_2H_4 \cdot TMED$[13] showed absorption

(13) G. E. Coates and P. D. Roberts, J. Chem. Soc. (A), 1008 (1969).

bonds at 1787 and 1807 cm^{-1}, while in $[(CH_3)_3NCH_3BeH]_2$ where the Be-H bonds are bridging, absorption occurs at 1342 cm^{-1}.[14]

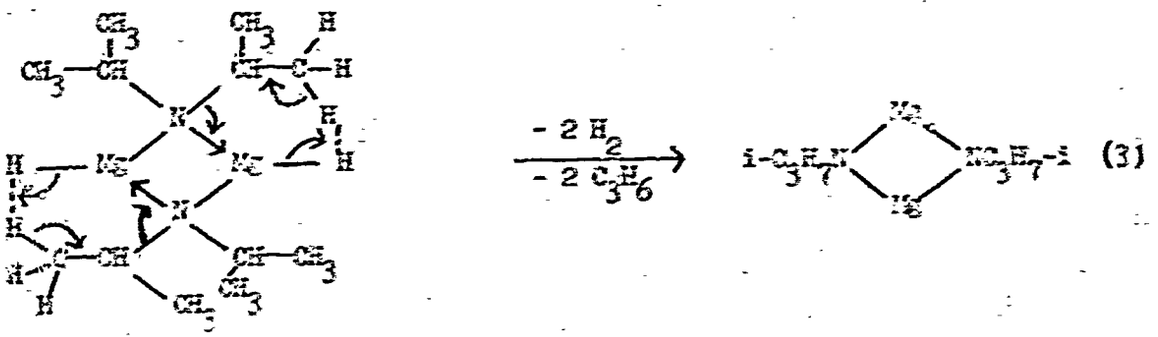
(14) G. E. Coates and N. A. Bell, J. Chem. Soc., 642 (1965).

Because of the low solubility of (I) no molecular weight determination was possible.

An attempt to prepare (I) from hydrogenation of a benzene solution of $C_2H_5MgN(i\text{-}C_3H_7)_2$ at 70° resulted in the formation of a compound with a different

X-ray powder pattern (Table 1). The Mg-H infrared bands were very broad and strong at 1590 and 655 cm^{-1}. The Mg:H molar ratio was 1.00:1.30 which may be due to some hydrogenation of the Mg-N bond to form MgH_2, although no MgH_2 lines were visible in the X-ray powder pattern. In this connection, the hydrogenation of $C_2H_5MgN(i\text{-}C_3H_7)_2$ at 110° resulted in complete hydrogenation of the Mg-N bond as well as the Mg-C bond to form MgH_2 exclusively. The fate of the amine was not determined.

The stability of (I) was studied in solution and in the solid state. A THF solution of (I) was refluxed overnight. The Mg:H ratio in solution decreased to 1.00:0.52. In the solid state (I) begins to decompose at 70° with a slow continuous weight loss to 300°. No strong endothermic or exothermic heat effects occurred. The weight loss to 300° corresponds closely to the loss of hydrogen and propene. A likely decomposition mechanism is a Hofmann type elimination of olefin from the amine as shown in (3).

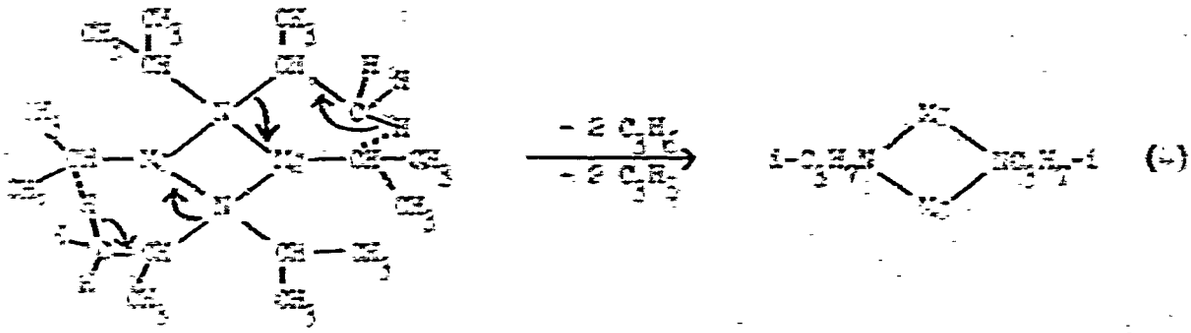


(3)

Although $(i\text{-}C_3H_7)_2NMgH$ is drawn as a dimer in (3) the same scheme would hold for a polymeric species with bridging hydrogens. The product in (3) continues to lose weight slowly above 300° with evidence of carbon being deposited on the

formate. Effluent gas analysis will be necessary to further describe the decomposition.

In order to gain more insight into the decomposition of (I), an attempt was made to prepare bis-diisopropylaminomagnesium, from $(i\text{-}C_3H_7)_2NH$ and $(i\text{-}C_3H_7)_2Mg$ in diethyl ether. After removing the solvent, the infrared spectrum showed amine still present (1625 cm^{-1}), and analysis of the residue showed that the compound was $i\text{-}C_3H_7MgN(i\text{-}C_3H_7)_2$. The failure to form the bis compound is probably due to steric factors since Coates,[14] found that $i\text{-}C_3H_7MgN(i\text{-}C_3H_7)_2$ could easily be desolvated while for example $C_2H_5MgN(i\text{-}C_3H_7)_2$ was impossible to desolvate. The thermal decomposition of $i\text{-}C_3H_7MgN(i\text{-}C_3H_7)_2$ was studied. An abrupt weight loss begins at 77° and continues without a break to 300°. This decomposition may proceed similar to (I) with the formation of propane by an attack of the isopropyl nucleophile from magnesium on the beta hydrogen of the isopropyl group of the amine and at the same time eliminating propene from the other leaving the same compound as (3). This would be similar to the case



reported by Coates[19] in which the pyrolysis of $[i\text{-}C_3H_7MgN(CH_3)CH_2CH_2N(CH_3)_2]_2$

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(18) G. E. Coates and J. A. Heslop, J. Chem. Soc. (A), 514 (1968).

gave propane instead of the expected propene. It is obvious from the gradual but continuous weight loss that dialkylaminomagnesium hydride could not be prepared from the pyrolysis of a dialkylaminomagnesium alkyl compound.

Di-n-butylaminomagnesium hydride [$(n\text{-}C_4H_9)_2NMgH$] (III) was synthesized by hydrogenation of $s\text{-}C_4H_9MgN(n\text{-}C_4H_9)_2$ at 25° similar to (I). (III) is soluble in benzene to the extent of 0.09 m/l and is very soluble in THF (> 0.8 m/l). (III) has only a slight solubility in diethyl ether. The infrared spectrum of (III) (Table 1) shows a strong MgH band at 1550 cm^{-1} and 650 cm^{-1}, and the X-ray powder pattern shows no lines for MgH_2. A preliminary molecular weight determination by the static vapor phase method indicates that (III) is dimeric in THF. The amino groups are probably in bridging positions with the hydrogens in terminal positions.

When a THF solution of (III) was refluxed overnight, the ratio of Mg:H decreased to 1.00:0.49. Thermal analysis shows that in the solid state (III) begins to lose a small amount of weight at 120°, but the most significant weight loss occurs beginning at 220° accompanied by an endothermic heat effect. The weight loss corresponds closely to the loss of hydrogen and butene leaving $C_4H_9N\begin{smallmatrix}Mg\\ \diagup\ \diagdown\\ Mg\end{smallmatrix}NC_4H_9$ which slowly continued to lose weight even above 500° Bis(di-n-butylamino)magnesium was synthesized and the thermal decomposition studied. Weight loss begins at 50° and continues gradually to 215°, where the rate of weight loss increases rapidly. The first weight loss corresponds to the loss of butene and the second to di-n-butylamine. The mechanism for the loss of butene is not clear. The total weight loss leaves a compound with a magnesium content the same as with (III).

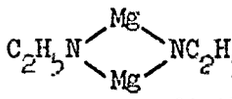
Hydrogenation of $C_2H_5MgN(n\text{-}C_4H_9)_2$ at 50° in benzene produced $(n\text{-}C_4H_9)_2NMgH$ of a different crystalline form (Table 1). The Mg:H ratio was 1.00:1.24. The Mg-H infrared bands occur at 1600 and 675 cm^{-1} in the solid state, but in THF (0.44M) the Mg-H stretching band occurs at 1500 cm^{-1}. The ratio of Mg:H in solution was 1.00:1.12.

An attempt to prepare (III) by $LiAlH_4$ reduction of $C_2H_5MgN(n\text{-}C_4H_9)_2$ in diethyl ether was unsuccessful because the products could not be separated. The infrared spectrum of the reaction product shows that the expected products were formed. No Al-H bands were observed in the 1600-1750 cm^{-1} region of the spectrum, but a Mg-H band at 1540 cm^{-1} was observed. (III) prepared in benzene by hydrogenation has very slight solubility in diethyl ether, but when formed in diethyl ether, it does not precipitate. Presumably (III) prepared in diethyl ether is an etherate which is soluble, but the stability of the desolvated crystalline lattice is such that resolvation does not occur.

An attempt to prepare (III) by a different route also failed. Di-n-butyl amine was added to a Grignard reagent to form di-n-butylaminomagnesium chloride ($(n\text{-}C_4H_9)_2NMgCl$). This compound was stirred several days with NaH both in benzene and diethyl ether. In both cases the starting compound was recovered unchanged.

Diethylaminomagnesium hydride $[(C_2H_5)_2NMgH]$ (IV) was synthesized by hydrogenation of $s\text{-}C_4H_9MgN(C_2H_5)_2$ similar to (I) (Table 1). IV is insoluble in benzene, however it is soluble in THF to the extent of 0.08 m/l. Thermal analysis of IV shows the principal weight loss begins at 200° and continues to 300° accompanied by a strong endothermic heat effect. The weight loss corresponds

to the loss of H_2 and C_2H_4 leaving a compound similar to that found in (3),



Bis-diethylaminomagnesium was synthesized for thermal analysis. Weight loss begins at 50° and continues gradually to 220° where an increase in the rate of weight loss begins accompanied by a slight endothermic effect. The first weight loss corresponds closely to the loss of ethylene while the second corresponds to the loss of diethyl amine. At 400° the residue from the decomposition of (IV) and bis-diethylaminomagnesium contains 35.82 and 35.53 per cent magnesium respectively assuming no loss of magnesium. This corresponds closely to the theoretical value calculated for (C_2H_5NMg), 36.08.

Diphenylaminomagnesium hydride ($(C_6H_5)_2NMgH$) (V) was synthesized in a similar manner as (I). (Table 1). (V) is only slightly soluble in benzene. Thermal analysis shows an endothermic heat effect at 220° with no weight loss. Above 350° a very slow weight loss begins. This decomposition is consistent with the proposed elimination of alkene from the amine. In this case elimination cannot occur with the phenyl groups and no weight loss occurs until a very high temperature is reached. At 220° the compound may decompose forming no volatile compounds.

Trimethylethylenediaminomagnesium hydride [$(CH_3)_2NCH_2CH_2N(CH_3)MgH$] (VI) was synthesized by the hydrogenation of $C_2H_5MgN(CH_3)CH_2CH_2N(CH_3)_2$ in benzene (Table 1). (VI) is soluble in benzene to the extent of 0.13 m/l. VI is unstable in refluxing benzene over a period of several days. An attempt to purify a sample by Soxhlet extraction resulted in loss of hydridic activity. The decomposition probably proceeds similarly to the above decompositions by a hydride attack on the amino methyl groups.

An attempt was made to prepare (VI) by the direct reaction of trimethylethylenediamine and MgH_2 similar to the reaction of trimethylethylenediamine and BeH_2 reported by Coates.[3] No reaction occurred at room temperature but on refluxing several days approximately one half of the MgH_2 reacted. However no hydridic activity was found in solution presumably because of the thermal decomposition of the hydride. Evaporation of the solvent gave a brown oily resin.

MgH_2 and diisopropylamine and di-n-butylamine did not react even under forcing conditions to form the hydrides. In all cases unreacted MgH_2 was recovered.

No attempt has been made to prepare the dimethylaminomagnesium hydride because the starting compound $RMgN(CH_3)_2$ is unstable and disproportionates to R_2Mg and $[(CH_3)_2N]_2Mg$.[10]

In contrast to the stable aminomagnesium hydrides, the alkoxymagnesium hydrides are unstable and disproportionate to MgH_2 and dialkoxymagnesium. The X-ray powder patterns (Table 2) for "ROMgH" (R = CH_3, i-C_3H_7, t-C_4H_9, C_6H_5) all show lines of MgH_2, and in addition, the remaining lines are those of the appropriate $(RO)_2Mg$ also listed in Table 2.

The synthesis of ROMgH compounds was attempted by two methods, direct reaction of MgH_2 and ROH and hydrogenation of RMgOR compounds. Although the MgH_2 used was an active form prepared by $LiAlH_4$ reduction of $(C_2H_5)_2Mg$ in diethyl ether, the direct reaction with alcohols was slow and proceeded only under refluxing conditions in THF or benzene. Apparently the reaction formed the intermediate "ROMgH" compound which then disproportionated to MgH_2 and $(RO)_2Mg$.

$$MgH_2 + ROH \rightarrow ROMgH + H_2 \qquad (5)$$

$$ROMgH \rightarrow 1/2\ MgH_2 + 1/2\ (RO)_2Mg \qquad (6)$$

Hydrogenation of $C_2H_5MgOt\text{-}C_4H_9$ at 110° in benzene resulted in the formation of a mixture of MgH_2 and $(t\text{-}C_4H_9O)_2Mg$ (Table 2). Since the disproportionation may be occurring at the higher temperature it was considered desirable to synthesize the compound at a lower temperature. $i\text{-}C_3H_7MgOt\text{-}C_4H_9$ was synthesized and hydrogenated at room temperature. No reaction occurred at room temperature, and the hydrogenation was repeated at 50°. A product was isolated and shown to be a mixture of MgH_2 and $(t\text{-}C_4H_9O)_2Mg$ by X-ray powder patterns.

$(RO)_2Mg$ compounds were synthesized in the same manner using two equivalents of alcohol. All of the $(RO)_2Mg$ are insoluble in the solvents used, benzene and THF. The phenol case is somewhat complicated by the formation of different crystalline forms from different solvents.

The infrared spectra of "ROMgH" and $(RO)_2Mg$ are identical. In a mixture the very broad weak bands of MgH_2 are not evident in the spectra. However, in no case was there any indication of MgH bands similar to the MgH bands found for the amino compounds.

The Preparation of $KMgH_3$ and Related Compounds

R. A. Kovar and E. C. Ashby

Abstract

$KMgH_3$ and related complex metal hydrides of magnesium have been prepared by hydrogenolysis or pyrolysis of $KMg(s\text{-}Bu)_2H$. The stable $KMgR_2H$ compounds were prepared from KH and MgR_2 in hydrocarbon solvent.

Introduction

The importance of complex metal hydrides of aluminum and boron (e.g., $LiAlH_4$ and $NaBH_4$) in both organic and inorganic chemistry is well known.[1]

(1) N. G. Gaylord, "Reductions with Complex Metal Hydrides," Interscience Publishers, New York, 1956.

Complex metal hydrides of alkali metals with magnesium, although highly sought after, are unknown. For example, in an attempt to prepare $LiMgH_3$, Tanaka[2]

(2) J. Tanaka and R. Westgate, Abstracts of Papers No. 155, 157th National ACS Meeting, 1969.

reported that hydrogenolysis of a mixture of methyllithium and dimethylmagnesium at elevated temperatures formed a mixture of LiH and MgH_2. Coates[3] recently

(3) G. E. Coates and J. A. Heslop, J. Chem. Soc. (A), 574 (1968).

reported that pyrolysis of the n-butyllithium adduct of dimethylmagnesium (presumably $LiMg(CH_3)_2C_4H_9$) formed a mixture of LiH and dimethylmagnesium.

Results and Discussion

We wish to report the first successful synthesis of a complex metal hydride of an alkali metal and magnesium. The compound $KMgH_3$ (potassium trihydridomagnesiate) was prepared by the hydrogenolysis of $KMg(s\text{-}C_4H_9)_2H$ in benzene solution.[4]

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(4) E. C. Ashby and R. C. Arnott, J. Organometall. Chem., (in press).

$$KMg(s\text{-}C_4H_9)_2H \xrightarrow{H_2} KMgH_3 + 2\ C_4H_{10} \qquad (1)$$

The solubility of $KMg(s\text{-}C_4H_9)_2H$ in benzene is unique and avoids the necessity of hydrogenolysis in more basic solvents, such as ethers, thus eliminating the competition between solvent and hydride ion for coordination sites in the expected product. In addition, secondary butyl groups bonded to relatively electropositive metals are known to undergo hydrogenolysis under relatively mild conditions. This factor allows reduction of this compound at room temperature where it is known to exist as an authentic $KMgR_2H$ complex. This is an important point since high temperature hydrogenation of Lewis acid-base complexes of this type might be preceded by extensive dissociation at the higher temperatures, followed by reduction forming a mixture of alkali metal hydride and magnesium hydride according to Eq. 2.

$$KMgR_2H \rightleftharpoons KH + MgR_2 \xrightarrow{H_2} KH + MgH_2 + 2\ RH \qquad (2)$$

Hydrogenolysis of a 0.5 molar benzene solution of potassium di-s-butylhydridomagnesiate (K:Mg:Butyl:H = 1.0:1.0:1.9:0.95) under 3000 psig hydrogen pressure at 25° for 4 hr. resulted in quantitative precipitation of a yellow solid which reacted violently when exposed to the atmosphere. This solid was analyzed for alkali metal (by flame photometry), magnesium (by EDTA titration) and hydrogen (by gas evolution analysis). Analysis gave a potassium, magnesium and hydrogen ratio of 1.0:1.0:3.0 (Anal. Calcd. for $KMgH_3$: K, 58.7, Mg, 36.8; H, 4.52. Found: K, 58.9; Mg, 36.2; H, 4.56). No butane was produced on hydrolysis indicating complete reduction and formation of a $KH{\cdot}MgH_2$ species. These analytical data are also consistent with the formation of a physical mixture of KH and MgH_2. However, X-ray powder analysis (Table I) revealed a unique diffraction pattern, different from the patterns for KH and MgH_2 indicating that the reaction product is not a physical mixture. The strongest line for KH (at 3.30 Å) and strongest lines for MgH_2 (at 3.19, 2.495, 1.67, and 1.59 Å) are nearly absent from the $KMgH_3$ pattern. Preliminary studies on $KMgH_3$ indicate that it is insoluble in common hydrocarbon and ether solvents, stable to disproportionation and does not cleave ether solvents. A preliminary study of the thermal properties of $KMgH_3$ as determined by simultaneous DTA-TGA analysis revealed a weak, broad exothermic effect at ~300°C which may indicate disproportionation to KH and MgH_2 followed by endothermic effects at 320 and 420°C due to decomposition of MgH_2 and KH respectively. $KMgH_3$ was also prepared by a pyrolytic olefin elimination reaction when $KMg(s\text{-}C_4H_9)_2H$ was heated in light mineral oil at 80° under vacuum.

$$KMg(s\text{-}C_4H_9)_2H \xrightarrow{\Delta} KMgH_3 + 2\ C_4H_8 \qquad (3)$$

Comparison of the powder pattern data for $KMgH_3$ with that of $KMgF_3$ suggests that these two compounds are isomorphous, a result predicted from the similar ionic radaii of F^- and H^-. The Perovskite structure was demonstrated for $KMgF_3$[5] and is thus implied for $KMgH_3$. This structure is found for ABX_3

(5) R. C. De Vries and Rustum Roy, J. Am. Chem. Soc., 75, 2479 (1953).

systems (A = B = metal cations, X = anion) in which one cation is much larger than the other. It is described as a cubic close-packed arrangement of the anions and the larger cations, with the smaller cations occupying octahedral positions in an ordered pattern.[6] It is proposed that each magnesium cation of

(6) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," John Wiley and Sons, Inc., New York, 1964, p. 668.

$KMgH_3$ is surrounded by an octahedral arrangement of hydride ions. The crystal structure of MgH_2 was clearly shown[7] to be that of rutile which also involves

(7) K. M. Mackay, "Hydrogen Compounds of the Metallic Elements," Wilmer Brothers Limited, Birkenhead, Cheshire, 1966, p. 40.

an octahedral array of hydride ions about each magnesium cation. The environment about magnesium in $KMgH_3$ and MgH_2 is therefore predicted to be essentially equivalent. Independent verification of this prediction is obtained from comparison of the infrared spectra (obtained as a Nujol mull between KBr salt plates) for these two compounds. MgH_2 exhibits two broad adsorption envelopes centered at 1160 and 650 cm^{-1}. These are assigned to metal-hydrogen stretching

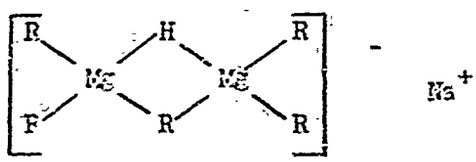
and deformation vibrations respectively. The infrared spectrum of $KMgH_3$ revealed two similarly broad adsorptions centered at 1150 and 680 cm^{-1}. The absence of pronounced shifts is verification of nearly equivalent environments in these compounds.

This study was extended to include reductions of the NaH-$(s\text{-}Bu)_2Mg$ system. It has been shown that 0.5 mol. of NaH (per mole of di-s-butylmagnesium) goes into solution when equivalent molar quantities of NaH and di-s-butylmagnesium are stirred at 50° for 48 hr. in benzene solution:[8]

(8) R. Arnott and E. C. Ashby, unpublished results.

$$NaH + Mg(s\text{-}C_4H_9)_2 \rightarrow 1/2\ NaH + 1/2\ NaMg_2(s\text{-}C_4H_9)_4H \qquad (4)$$

Filtration of the reaction mixture allows separation of benzene soluble $NaMg_2R_4H$. The proposed structure is shown below.



Reduction of the secondary butyl groups was predicted to generate a $NaMg_2H_5$ species, mixtures of $NaMgH_3$ + MgH_2, or NaH + 2 MgH_2, depending on the relative stabilities of each.

Hydrogenation of this material at room temperature effected quantitative precipitation of magnesium and sodium. The solid was isolated and the sodium,

magnesium, and hydrogen atomic ratio found to be 0.9:2.0:4.0. No butane was evolved indicating complete reduction. Unfortunately, the X-ray powder pattern of this material did not show clear lines which would differentiate the possible products. This is attributed to the very small particle size of this material. Thermal analysis of this solid as determined by DTA-TGA studies, revealed a strong exothermic effect at 115° which may indicate intramolecular rearrangement of $NaMg_2H_5$ to $NaMgH_3$ and MgH_2. Subsequent effects in the thermal analysis are qualitatively consistent with pyrolysis of a mixture of $NaMgH_3$ and MgH_2. The solid obtained by heating this hydrogenation product past 115° exhibited clear X-ray powder diffraction lines which we attribute to $NaMgH_3$ and MgH_2 (Vide Infra).

Removal of solvent from $NaMg_2R_4H$ (R = s-butyl) under vacuum and pyrolysis in light mineral oil at 105° for several hours afforded a solid material, light gray in color. The X-ray diffraction pattern of this material contained strong, well defined lines (Table II). Several of the weaker lines correspond exactly to those reported for MgH_2. The remaining lines are assigned to $NaMgH_3$. These lines bear a remarkable resemblance (both in intensity and distribution) to those reported for $KMgH_3$ with the exception that lines in the latter compound occur at slightly larger d values owing to the larger K^+ ionic radius and larger unit cell parameters.

$$NaMg_2R_4H \text{ (R = s-butyl)} \xrightarrow[105^\circ]{\Delta} MgH_2 + NaMgH_3 \qquad (5)$$

The lines assigned to $NaMgH_3$ are very similar to those reported for $NaMgF_3$ (Table II), indicating that these two compounds are isomorphous and isostructural. The

perovskite structure was demonstrated for $NaMgF_3$ and is thus implied for $NaMgH_3$.

We are presently attempting to prepare $NaMg_2H_5$ by low temperature pyrolysis of Na_2MgR_4H (R = s-butyl) in the hope that we will obtain a product which will produce an interpretable X-ray powder diffraction pattern. (We have observed that in general, pyrolysis of a material affords solids with larger particle size, and consequently better defined powder pattern than that obtained by hydrogenation). We will then be in an excellent position to study the thermally induced disproportionation to $NaMgH_3$ and MgH_2.

Our results concerning attempts to prepare $LiMgH_3$ by room temperature hydrogenation of $LiMgR_3$ (R = s-butyl) in benzene solution are at present inconclusive. Hydrogenation of $LiMgR_3$ (R = s-butyl), made by mixing equal molar quantities of s-butyl lithium and di-s-butylmagnesium in benzene, afforded quantitative precipitation of lithium and magnesium and a solid which revealed a lithium, magnesium, and hydrogen ratio of 0.95:1.00:2.80. Unfortunately, the solid produced in this reaction was of very fine particle size and did not produce a well defined X-ray powder pattern. The broad and diffuse lines which were present correspond reasonably well with lines reported for MgH_2 and LiH, however one of these lines did not. It is thus possible that $LiMgR_3$ (R = s-butyl) exists in benzene solution in equilibrium with species which when subjected to hydrogenation produce a mixture of MgH_2, LiH, and $LiMgH_3$:

$$LiMgR_3 \rightleftharpoons RLi + MgR_2 \xrightarrow{H_2} LiMgH_3 + LiH + MgH_2 \qquad (6)$$

Thermal analysis of the hydrogenation product revealed a strong endotherm at 310° accompanied by loss of weight as hydrogen (90% of calculated). A weak

endotherm occurs at 480° accompanied by loss of weight as hydrogen (10% of calculated). The 480° endotherm is assigned to decomposition of LiH by comparison with the authentic thermogram for LiH. The effect at 310° must therefore correspond to simultaneous decomposition of MgH_2 and $LiMgH_3$. If this interpretation is correct then the mixture would consist of 33% of LiH and MgH_2 in admixture with $LiMgH_3$ 66%.

Plans for future research involve more definitive DTA-TGA studies of the presumed $LiMgH_3$, MgH_2, LiH mixture. Attempts will be made to prepare $LiMgH_3$, by chemical reduction of $LiMgMe_3$.

$$LiMgMe_3 + 3/4\ LiAlH_4 \rightarrow LiMgH_3 + 3/4\ LiAlMe_4$$

Chemical reduction of methyllithium, dimethylmagnesium adducts represents a versatile approach to $LiMgH_3$ since reduction can be attempted in a variety of ether solvents and at a variety of reaction temperatures. A logical approach involves reduction of 1:1 molar mixtures of methyllithium and dimethylmagnesium at low temperatures in THF solvent, since detailed spectral measurements[9] indicate

(9) L. M. Seitz and B. F. Little, J. Organometall. Chem., 18, 277 (1969).

predominant formation of $LiMgMe_3$ under these conditions. Complex equilibria between higher order methyllithium, dimethylmagnesium adducts and dimethylmagnesium exist at higher temperatures in THF or in weaker ether solvents. Chemical reduction of these mixtures is predicted to form a variety of complex hydrides in admixture with MgH_2:

$$Li_2MgMe_4 + MgMe_2 \rightarrow Li_2MgMe_4 + MgH_2 \quad (7)$$

This work will logically be extended to include chemical reactions of higher order methyllithium, dimethylmagnesium adducts under conditions which are known to favor formation of these adducts.

$$Li_nMgR_{2+n} + \frac{2+n}{4} LiAlH_4 \rightarrow Li_nMgH_{2+n} + \frac{2+n}{4} LiAlR_4 \quad (8)$$

n = 2 and 3

The conditions which were found[9] to have an influence on the equilibria between methyllithium, dimethylmagnesium adducts in solution are: 1) the initial lithium and magnesium molar ratio, 2) the base strength of the solvent employed and 3) the temperature of the solution.

Table I. X-Ray Pattern Data[a]

KH		MgH_2	$KMgH_3$	$KMgF_3$[2]
3.30	V.S	3.19 VS	4.003 VW	
2.86	S	2.76 VW	3.137 VVW	
2.02	S	2.495 VS	2.835 VS	2.80 M
1.7?	S	2.29 M	2.311 M	2.29 M
1.43	M	1.59 S	2.007 S	1.99 VS
1.65	M	1.67 S	1.794 VW	
1.31	M	1.50 M	1.639 S	1.625 M
1.28	M	1.42 W	1.420 M	1.408 M
1.17	M	1.36 W	1.268 M	1.259 W
1.10	M	1.335 W	1.184 M	1.201 S
1.01	W	1.246 W	1.158 W	1.150 W
		1.150 W	1.122 VW	
		1.125 W		

[a] X-ray powder diffraction data were obtained using a Phillips Norelco X-ray Unit, using an 11.46 cm. diameter camera with Ni-filtered CuK_α radiation. Line intensities were estimated visually.

Table II. X-Ray Powder Pattern Data

NaH		$NaMgF_3$[10]		$NaMgH_3$ and MgH_2 (Mixture)	
d	I	d	I	d	I
2.83	S	3.83	M	3.85	VW
2.44	S				
1.73	S	2.71	M	3.16*	VW
1.47	S	2.30	W	3.00	W
1.41	M	2.23	W	2.83	VVW
1.22	M	2.20	VW	2.75	VS
1.12	M	1.92	VS	2.50*	W
1.09	M	1.58	VW	2.26	W
0.939	M	1.55	W	1.92	W
0.863	W	1.35	VW	1.67*	W
0.825	M			1.56	M
0.813	M			1.35*	W
				1.21*	W
				1.11	W
				1.03	W

*Lines due to MgH_2 (See Table I).

(10) E. Chao, Et. Al., The American Minerologist, 16, 379 (1931).

Direct Preparation of Aminoalanes

R. A. Kovar and E. C. Ashby

Abstract

Detailed studies of the synthesis of aminoalanes by the direct reaction of aluminum, hydrogen, and secondary amines are reported. The reaction was studied most thoroughly with diethylamine. Tris- and bis(diethylamino)alanes could be prepared in high yield depending on the reaction conditions and on the initial amine to aluminum molar ratio. Reaction of aluminum and diethylamine in molar ratios ranging from 1:1 to 2:1 at 150° afforded high yields of bis(diethylamino)alane ($HAl[N(C_2H_5)_2]_2$). Low yields of diethylaminoalane ($H_2AlN(C_2H_5)_2$) were generated in admixture with bis(diethylamino)alane when the reaction temperature was lowered, the maximum yield of diethylaminoalane was found to be 15% at 65°.

The study was extended to include the reaction of dimethyl-, di-i-propyl, and di-phenylamine, pyrrolidine, and piperidine with excess aluminum and hydrogen. As with diethylamine, predominant formation of the bis(dialkylamino)alane was observed with dimethylamine, piperidine and pyrrolidine. No reactions were observed with di-i-propyl- and di-phenylamine.

Predominant formation of bis(dialkylamino)alanes in preference to dialkylaminoalanes is attributed to greater thermodynamic stability of the former compounds. This was verified by detailed studies of the thermal pyrolysis of the dialkylaminoalanes. DTA-TGA, neat sealed tube and solution pyrolysis studies indicate the following decomposition reaction:

$$2\ H_2AlNR_2 \rightarrow HAl(NR_2)_2 + Al\downarrow + 3/2\ H_2\uparrow$$

Proton magnetic and infrared spectral measurements of the aminoalanes are reported and interpreted to yield valuable analytical and structural information.

Introduction

Aminoalane compounds ($H_{3-n}Al(NR_2)_n$, n = 1, 2) are used as polymerization catalysts,[1] reducing agents,[2] and as synthetic intermediates,[3] however more widespread use of these compounds is limited by the inconvenience of preparation and high cost of these reagents. Until now aminoalanes have been prepared by the reaction of (1) alane[4] or trimethylamine alane[5] with secondary amines (eq. 1) and (2) lithium aluminum hydride and dialkylammonium chlorides[6] (eq. 2).

(1) S. A. SNAM, Belgian Patent 654,406, April 15, 1965.

(2) S. Cesca, M. Santoslasi, W. Marconi, and N. Palladino, Annal. di Chimica (Rome), SS 704 (1965).

(3) H. Nöth and E. Wiberg, Fortschr. Chem. Forsch., 8 323 (1967).

(4) E. Wiberg and A. May, Z. Naturforshung, B10, 234 (1955).

(5) W. Marconi, A. Mazzei, F. Bonati, and M. de Malde, Gazze. Chim. Ital., 92 1062 (1962).

(6) John K. Ruff, J. Am. Chem. Soc., 83 2835 (1961).

$$AlH_3 + nHNR_2 \rightarrow nH_2 + H_{3-n}Al(NR_2)_n \quad n = 1, 2, \text{ and } 3 \qquad (1)$$

$$LiAlH_4 + R_2NH_2Cl \rightarrow LiCl + 2\,H_2 + H_2AlNR_2 \qquad (2)$$

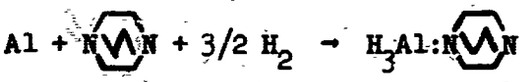
We wish to report in full[7] our findings concerning the direct preparation

(7) A preliminary report concerning this study is in press in J. Organometall. Chem.

of aminoalanes by the reaction of aluminum, secondary amines and hydrogen under mild conditions. This route to aminoalanes was predicted on the basis of earlier studies[8] of the direct preparation of triethylenediamine alane by the reaction

(8) E. C. Ashby, J. Am. Chem. Soc., 86, 1882 (1964).

of the tertiary amine, aluminum, and hydrogen under mild conditions.



(3)

The reaction of a secondary amine, aluminum, and hydrogen was predicted to follow an analogous path involving intermediate formation of AlH_3 followed by complexation of the secondary amine to form $AlH_3{:}NR_2H$. Since secondary amine-alanes are unstable and lose hydrogen well below room temperature,[3] the dialkylaminoalanes are the first products which were predicted. In the presence of additional secondary amine the dialkylaminoalane was predicted to react and form the bis(dialkylamino)alanes and in presence of additional dialkylamine, the tris(dialkylamino)alane.

(4)

Experimental

Equipment and Materials. - Manipulation of air sensitive materials was accomplished by use of standard bench top techniques[9] or employment of a dry box equipped with an atmosphere purification system for removal of oxygen and moisture.[10]

(9) D. F. Schriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill Book Company, New York, N. Y. 1969.

(10) T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, Rev. Sci. Instr., 33, 491 (1962).

Infrared spectral measurements were obtained using a Perkin Elmer 621 Automatic Grating Spectrophotometer. Samples were prepared for analysis in the dry box. Spectra of liquid samples were obtained from analysis of the neat material between KBr salt plates while spectra of solid samples were obtained as the Nujol mull. Proton magnetic resonance spectra were obtained using a Varian A-60 magnetic resonance instrument using the solvent signal (benzene) as internal standard.

Hydrogenation reactions were performed using a 300 ml. Magnedrive Autoclave Unit (Autoclave Engineers, Inc.). The chamber was usually charged in the dry box. The contents were then heated under hydrogen for a predetermined period of time. After sufficient cooling the chamber was vented and soluble products filtered from excess unreacted aluminum in the dry box.

Benzene, used as the solvent in the hydrogenation reactions, was purchased from Fisher Chemical Co. (Certified ACS Grade) and distilled from $NaAlH_4$ prior to use. Dimethylamine (anhydrous) was purchased from the Matheson Corporation and passed through a KOH drying tube prior to use. Diethyl-, di-i-propyl-,

diphenylamine, piperidine, and pyrrolidine were purchased from Eastman Chemical Co. The liquid dialkylamines were either distilled from anhydrous KOH or distilled onto active molecular sieve Type 4-A prior to use. Diphenylamine was used without further purification. Aluminum powder (600 mesh) was obtained from the Alcan Aluminum Corporation. Aluminum was "activated" prior to use by the Ziegler activation process.[11] Ultra Pure Hydrogen (99.9995%) was

(11) E. C. Ashby, G. J. Brendel and H. E. Redman, Inorg. Chem., 2, 499 (1963).

obtained from the Matheson Corp. and used without further purification.

Analyses. - Aminoalanes are readily hydrolyzed by water and dilute acids. Analyses were performed by hydrolyzing a tared sample with a water-acid mixture and determination of the hydrogen content by gas evolution analysis. Aluminum in the same sample was determined by EDTA titration. Amines were determined by potentiometric titration of the solution obtained on hydrolysis of a tared sample after removal of the $Al(OH)_3$.

Direct Preparation of $Al(NEt_2)_3$. - Aluminum (2.7 gr or 0.1 mol.) and diethylamine (100 ml.) were stirred and heated at 150° under 3000 psig hydrogen for 4 hr. Removal of solvent (after filtration to remove traces of unreacted aluminum metal) under vacuum gave 21 gr. or 91% yield of $Al(NEt_2)_3$ (Rctn. 8, Table I). Anal. Calc. for $Al(NEt_2)_3$: Al, 11.1; amine, 88.9. Found: Al, 12.8; amine, 87.6. Infrared spectral analysis (Nujol mull) was identical to that of the authentic complex prepared by the reaction of trimethylamine alane in boiling diethylamine.

Direct Preparation of $HAl(NEt_2)_2$.

A. From Equal Molar Quantities of Aluminum and Diethylamine. - Aluminum

(2.7 gr. or 0.10 mol.), diethylamine (10 ml. or 0.10 mol.) and benzene (100 ml.) were stirred and heated at 150° under 4000 psig hydrogen for 3 hr. Vacuum distillation of solvent (after filtration in the dry box to remove traces of unreacted aluminum) gave 15.8 gr. or 92% yield of $HAl(NEt_2)_2$ (Rctn. I, Table I). Anal. Calc. for $HAl(NEt_2)_2$: Al, 15.7; amine, 83.8; H, 0.582. Found: Al, 16.0; amine, 84.4; H, 0.612. The infrared spectrum of this material (neat between KBr plates) was identical to that of the authentic material prepared from unequivocal synthesis (vide infra).

B. From Excess Aluminum and Diethylamine. - Aluminum (5 gr. or 0.185 mol.) diethylamine (10 ml. or 0.10 mol.) and benzene (100 ml.) were stirred and heated under 4000 psig H_2 at 150° for 3 hr (Rctn. 2, Table I). The mixture was allowed to cool and filtered in the dry box to remove excess unreacted aluminum. The solution was made up to a known volume and analyzed. The hydrogen, aluminum, and nitrogen ratio was found to be 0.98:1.0:1.95. The infrared spectrum of the solute (obtained by removal of solvent under vacuum) was identical to that of authentic $HAl(NEt_2)_2$. The yield was 98%.

Direct Preparation of $H_2Al(NEt_2)$ in admixture with $HAl(NEt_2)_2$. - The reaction was run exactly as in B. above except that the reaction temperature was lowered to 65° and reaction time extended to 24 hr (Rctn. 6, Table I). Analysis of the solution after filtration gave a hydrogen and aluminum ratio of 1.13 to 1.00, indicating a low yield of $H_2Al(NEt_2)$ in admixture with $HAl(NEt_2)_2$. Yields (based on this analysis) were H_2AlNEt_2 15%, HAl(NEt) 78%. The proton magnetic resonance spectrum of this mixture in benzene solution had signals which were consistent with a simple physical mixture of mono- and bis(diethylamino)alanes (Table V).

Direct Preparation of Bis(piperidino)alane and (piperidino)alane. - Aluminum (5 gr.), piperidine (0.10 mol.) and benzene (100 ml.) were stirred at 110° under 4000 psig hydrogen for 20 hr (Rctn 5, Table II). A solid (9.1 gr.) product was isolated after filtration and removal of solvent under vacuum. Analysis of this solid revealed a hydrogen and aluminum ratio of 1.1:1.0 indicating predominant formation of the bis(dialkylamino)alane. A small amount (0.4 gr. yield = 3.5%) of $H_2AlNC_5H_{10}$ was sublimed when this product was heated at 65° and 1 mm. The remainder of the product (8.7 gr) was found to be $HAl(NC_5H_{10})_2$ (89% yield). Anal. Calc. for $H_2AlNC_5H_{10}$: H, 1.8; Al, 23.9; amine, 74.3. Found: H, 1.6, Al, 21.9; amine, 77.5. Calc. for $HAl(NC_5H_{10})_2$: H, 0.51; Al, 13.8; amine, 85.7. Found: H, 0.53; Al, 13.8; amine, 85.7. Proton magnetic resonance spectra of these products in benzene solution and infrared spectra of the solids were found to be identical with those of the corresponding aminoalane prepared by unequivocal synthesis.

Direct Preparation of $HAl(NMe_2)_2$. - Aluminum (5 gr.) and benzene (100 ml.) were transferred into the autoclave chamber. Dimethylamine (0.10 mol.) was vapor transferred into the chamber cooled in a dry ice acetone slurry. These reagents were heated at 150° under 3000 psig hydrogen for four hours (Rctn. 1, Table II). Solid product was isolated by filtration and removal of solvent under vacuum. Analysis of this solid gave a hydrogen to aluminum ratio of 1.0:1.0 indicating formation of the bis(dimethylamino)alane. Anal. Calc. for $HAl(NMe_2)_2$: H, 0.863; Al, 23.2; amine, 75.9. Found: H, 0.93; Al, 24.6; amine (by difference) 74.9. Yield was 10.5 gr. or 91%.

Direct Preparation of $HAl(NC_4H_8)_2$. - Aluminum (5 gr.), pyrrolidine (0.10 mol.), and benzene (100 ml.) were stirred and heated at 150° under 40000 psig hydrogen

for 12 hr. (Rctn 6, Table II). The product was isolated by filtration and removal of solvent under vacuum. Yield was 8.7 gr or 88%. Anal. for $HAl(NC_4H_8)_2$: Calc. Al, 16.1, amine, 87.4; H, 0.596. Found: Al, 15.0; amine, 84.3; H, 0.70.

Unequivocal Synthesis of Aminoalane Compounds. - Dialkylamino- and bis-(dialkylamino)alanes were prepared by the reaction of trimethylamine alane and one or two equivalents of an appropriate secondary amine, in benzene solution.[5] The solutions were usually heated at reflux for 2 hr. after initial mixing of the reagents. Products were isolated by removing the solvent under vacuum. These compounds were analyzed for hydrogen and aluminum and the experimental values were found to agree with the calculated values to within 5% in all cases. The following compounds were synthesized: H_2AlNEt_2, $HAl(NEt_2)_2$, $H_2AlNC_5H_{10}$, $HAl(NC_5H_{10})_2$, $H_2AlNC_4H_8$, $HAl(NC_4H_8)_2$, $H_2AlN(i\text{-}Pr_2)$, $HAl(N(i\text{-}Pr)_2)_2$.

Tris(dimethylamino)alane was prepared by the reaction of trimethylamine alane in benzene solution with excess dimethylamine. (Dimethylamine was allowed to bubble through the stirred alane solution at room temperature until liberation of hydrogen at the gas dispersion frit was observed to cease). Attempts to prepare tris(diethylamino)alane by the reaction of equimolar mixtures of bis-(diethylamino)alane and diethylamine by refluxing these reagents in benzene solution for as long as 12 hr. failed as evidenced by the fact that hydridic hydrogen was always found in solution. The reaction could be forced to completion by the reaction of bis(diethylamino)alane in diethylamine for 12 hr. at reflux temperature. Tris(piperidino)alane was prepared in an analogous way by the reaction of trimethylamine alane and ~10 fold excess piperidine in benzene.

Pyrolysis Studies of Aminoalane Compounds. -

A) Pyrolysis of $H_2AlNC_5H_{10}$ in Refluxing Toluene. - Piperidinoalane (1.68 gr.

or 9.6 mmol.) was dissolved in 30 ml. toluene and heated at reflux. Aliquot samples (2.0 ml.) were withdrawn at appropriate intervals with a syringe. Toluene was removed under vacuum and the solid thus obtained dissolved in 0.5 ml. benzene, (toluene had to be removed since methyl resonance of toluene was found to interfere in the proton magnetic resonance study) and proton magnetic resonance spectra of the samples recorded. These spectral data are shown in Figure I. The spectral changes were complete after heating for 8.5 days. After this period of heating the aluminum and hydrogen ratio was found to be 1.0 to 1.1. A dark grey, metallic precipitate (presumed to be aluminum) formed during this period.

B) DTA-TGA Analysis of Aminoalanes. - The thermal behavior of H_2AlNR_2 and $HAl(NR_2)_2$ compounds (NR_2 = NEt_2, NC_5H_{10}, NC_4H_8) was studied by simultaneous differential thermal and thermal gravimetric analysis of these compounds using Mettler Thermoanalyzer II instrumentation. Samples were loaded into tared platinum crucibles in the dry box. These were subjected to pyrolysis on the DTA-TGA instrument under a steady flow of argon. Representative thermal data obtained from analysis of $H_2AlNC_5H_{10}$ and $HAl(NC_5H_{10})_2$ are shown in Figure II. The bulk of the thermal properties are summarized in Table III.

C) Pyrolysis of H_2AlNR_2 Compounds in Evacuated, Sealed Tubes. - Piperidinoalane (0.1247 gr. or 1.107 mmol.) was sealed in an evacuated break seal bulb of approximately 20 ml. volume. The entire assembly was submerged into a 200°C oil bath for 15 minutes and allowed to cool. The tube was attached to a vacuum manifold by means of an "O" ring gasket seal and hydrogen (0.755 m mol.) determined by gas evolution analysis after opening the break seal with a magnet. Residual solid was dissolved in benzene and the proton magnetic resonance spectrum of the resulting solution was recorded. This spectrum was found to be identical to that of authentic

(piperidino)alane. (Figure III).

Hydrogen (1.1 m mol.) was isolated in an analogous experiment by heating diethylaminoalane (0.1531 gram or 1.516 m mol.) at 180° for 15 minutes. A dark grey metallic precipitate (assumed to be aluminum) formed during each of these pyrolyses.

Results and Discussion

The reaction of aluminum and hydrogen was studied in most detail with diethylamine and the results are summarized in Table I. Bis(diethylamino)alane

[Place Table I here.]

was the only compound formed when equivalent quantities of aluminum and diethylamine were heated under hydrogen pressure for 3 hr. (Reaction 1 - Table I). The product from this reaction was isolated and analyzed successfully for $HAl(NEt_2)$. The proton magnetic resonance spectrum (in benzene) and infrared spectrum were identical to spectra of the analogous product prepared by unequivocal synthesis.

$$2\ H_2 + 2\ Al + 4\ HNEt_2 \rightarrow 2\ HAl(NEt_2)_2 + 3\ H_2 \qquad (5)$$

Efforts to prepare diethylaminoalane by increasing the aluminum to diethylamine molar ratio (Reaction 2) and extending reaction times (Reactions 3, 4, and 5) were largely unsuccessful. The hydrogen and aluminum ratio in the products obtained in these reactions was always slightly higher than unity indicating a low yield of the diethylaminoalane. (Yields ranged from 3 to 9%). These results indicate that the reaction of aluminum, hydrogen and bis(diethylamino)alane to form diethylaminoalane does not occur to any appreciable extent at 150°.

Table I. Reactions of Aluminum, Hydrogen, and Diethylamine in Benzene Solvent

$$Al + 3/2\ H_2 + n(Et_2NH) \xrightarrow{\Delta, P} H_{3-n}Al(NEt_2)_n + nH_2$$

n = 1, 2, and 3

Rctn #	Molar Ratio Al:Amine	(H_2-P)	Time hr.	Temp. °C	Products and Yields	
1	1:1	4000	3	150	$HAl(NEt_2)_2$	92
2	Excess Al	4000	3	150	$HAl(NEt_2)_2$	98
3	Excess Al	3000	7	150	$HAl(NEt_2)_2$	86
					$H_2Al(NEt_2)$	9
4	Excess Al	3000	16	150	$HAl(NEt_2)_2$	91
					$H_2Al(NEt_2)$	4
5	Excess Al	3000	28	150	$HAl(NEt_2)_2$	90
					$H_2Al(NEt_2)$	3
6	Excess Al	4000	24	65	$HAl(NEt_2)_2$	78
					$H_2Al(NEt_2)$	15
7	1:4	3000	3	150	$HAl(NEt_2)_2$	5
					$Al(NEt_2)_3$	88
8	Excess Amine (Amine solvent)	3000	4	150	$Al(NEt_2)_3$	91

$$2\,Al + 3\,H_2 + 2\,HAl(NEt_2)_2 \xrightarrow{150^\circ} 4\,H_2AlNEt_2 \qquad (6)$$

Reaction at 65° produced a material which revealed a hydrogen to aluminum ratio of 1.1:1.0 indicating overall yields of bis(diethylamino)alane and diethylaminoalane in the ratio 78:15. These data suggest that $HAl(NEt_2)_2$ is thermodynamically more stable than H_2AlNEt_2 and thus the former compound is produced in high yield under conditions predicted to form either H_2AlNEt or $HAl(NEt_2)_2$. This was verified by pyrolysis studies of diethylaminoalane (vide infra).

It is interesting to note that even at an aluminum to amine ratio of 1:4 some (5%) $HAl(NEt_2)_2$ remained in admixture with $Al(NEt_2)_3$; however, the latter compound was produced in high yield (91%) when diethylamine was used as the solvent. These results suggest that forcing conditions are required to prepare tris(dialkylamino)alanes, due presumably to steric crowding in the product. This conclusion was substantiated by our attempts to prepare $Al(NEt_2)_3$ by the reaction of equivalent molar quantities of $HAl(NEt_2)_2$ and diethylamine in benzene solution. The replacement of all hydridic hydrogen was incomplete even after refluxing for 12 hr. The reaction could only be forced to completion by using diethylamine as the solvent and refluxing for 12 hr.

The most encouraging results observed in the reaction of aluminum, hydrogen, and diethylamine were obtained in the reaction of excess aluminum with diethylamine. The conditions for preparation of $HAl(NEt_2)_2$ in high yield were extended to the reaction of aluminum and other secondary amines. A variety of amines were chosen based on their relative base strengths as determined by both electronic and steric factors. These included dimethyl-, di-i-propyl- and diphenylamine, piperidine and pyrrolidine. The results of these experiments are summarized in Table II.

[Place Table II here.]

Table II. Reactions of Excess Aluminum, Hydrogen and Selected Dialkylamines in Benzene Solvent

$$Al + 3/2\ H_2 + R_2NH \xrightarrow{\Delta, P}$$

Rctn #	Molar Ratio Al:Amine	Amine	P(H_2)	Rctn. Time (hr.)	Rctn. Temp. °C	Products and Yield	
1	1.5:1 (Excess Al)	$HNMe_2$	3000	4	150	$HAl(NMe_2)_2$	91
2	"	"	4000	20	110	$HAl(NMe_2)_2$	72
						$H_2Al(NMe_2)$	18
3	"	"	4000	20	60	No Reaction	
4	"	piperidine	4000	5	180	$H_2AlNC_5H_{10}$	0.9
						$HAl(NC_5H_{10})_2$	83
5	"	"	4000	20	110	$H_2AlNC_5H_{10}$	3.5
						$HAl(NC_5H_{10})_2$	89
6	"	pyrrolidine	4000	12	150	$HAl(NC_4H_8)_2$	88
7	"	$HN(i\text{-}Pr)_2$	4000	4	110	No Reaction	
8	"	$HN(\phi)_2$	3000	4	150	No Reaction	

As was the case with dimethylamine, predominant formation of the bis-(dialkylamino)alane was observed by reaction of aluminum in excess with dimethylamine (Reaction 1), piperidine (Reaction 4), and pyrrolidine (Reaction 6). Low yields of the dialkylaminoalane were observed when these reactions were run at lower temperature (Reactions 2, 5). No reaction was observed in attempts to prepare H_2AlNMe_2 at 60° (Reaction 3).

No reaction was observed when the secondary amine was di-i-propylamine or diphenylamine, indicating that the base strength of the secondary amine is an important factor in the direct preparation reaction. Either AlH_3 is not generated by the reaction of aluminum and hydrogen in the presence of weak secondary amines or AlH_3 is generated but the reaction with these secondary amines is not sufficiently fast to compete with the thermal autodecomposition of the AlH_3.

Thermal Properties of Aminoalane Compounds. - The direct preparation study suggests that bis(dialkylamino)alanes are thermodynamically more stable than the corresponding dialkylaminoalanes and thus the former compounds are formed preferentially at these reaction temperatures. We sought to obtain independent verification of these observations. Little information is available concerning the thermal stabilities of aminoalanes. Wiberg[4] reported that dialkylaminoalanes decompose upon heating above their melting points with precipitation of dark flakes. No details concerning this pyrolysis were reported and the exact products of decomposition are unknown. Mösth[3] suggested that expected decomposition products might include H_2, Al, $HAl(NR_2)_2$, or $Al(NR_2)_3$, etc. On the other hand, it is known that the corresponding bis(dialkylamino)alanes are quite stable thermally. Thus, it has been reported that bis(dimethylamino)- and bis(di-i-propylamino)alane can be heated under normal pressure with refluxing, without decomposition.[3]

The thermal decomposition of dialkylaminoalanes has been studied by quantitative determination of pyrolysis products under exact pyrolysis conditions. The pyrolysis of piperidinoalane was studied most thoroughly since this compound can be separated easily from possible decomposition products by sublimation. In addition, spectroscopic properties of this compound and predicted decomposition products are unique and can in fact be used to follow the pyrolysis reaction. It was hoped that results obtained from study of this system could be extended to describe pyrolysis of other dialkylaminoalanes.

In one pyrolysis experiment, piperidinoalane was heated at reflux in toluene. Aliquot samples were withdrawn at appropriate intervals and the solvent removed under vacuum, replaced by benzene, and the proton magnetic resonance spectrum of the benzene solution recorded. These data are summarized in Figure I. The initial (T = 0) spectrum of piperidinoalane is changed considerably by heating at 110° for 2.5 days. The hydride signal of this compound at 5.76 τ is broadened considerably and a new signal (triplet at 6.80 τ) appears. The pyrolysis was continued by refluxing for longer periods. After 6.5 days the signal due the hydridic proton was no longer present and the signal at 6.80 τ was more intense. After heating at 110° for 8.5 days the area of the signal at 6.80 τ was found to be equal to the area of the signal at 7.10 τ and the spectrum at this point is identical to that of bis(piperidino)alane (see Figure III). These spectral data were found to be insensitive to further heating. The aluminum and hydrogen ratio was determined for an aliquot and found to be 1:1. A grey precipitate (assumed to be aluminum) formed during this pyrolysis. This spectral study of the aminoalane decomposition is qualitative, but does suggest that the soluble species formed is bis(piperidino)alane and that the pyrolysis reaction

stops with formation of this species. We propose the following pyrolysis reaction to account for these data.

$$2\ H_2AlNC_5H_{10} \rightarrow HAl(NC_5H_{10})_2 + 3/2\ H_2\uparrow + Al\downarrow \qquad (7)$$

Attempts were made to obtain quantitative characterization of this conversion by employing simultaneous gravimetric and differential thermal analysis. DTA-TGA thermal data obtained for mono- and bis(piperidino)alane are shown in Figure II. Piperidinoalane exhibited 3 endothermic effects at 60, 195 and 310°. The first is assigned to melting and corresponds to the reported melting point of 58°. The effect at 200 is tentatively assigned to conversion to the bis(piperidino)-alane, aluminum and hydrogen; however, the weight loss at this point was always found to be greater (by ~50%) than that predicted on the basis of the proposed pyrolysis reaction. Some material, however, was always found to "blow" out of the crucible and observed to collect on the inner surface of the furnace assembly. It was found that this extraneous weight loss could be diminished by using a crucible cover and heating at a slower rate, but it could never be stopped completely. The last endotherm (300°) is assigned to decomposition of bis-(piperidino)alane. This assignment is verified by the thermogram obtained for bis(piperidino)alane which exhibited, in addition to endothermic melting at 100°, a similar decomposition endotherm at 310°. The exact nature of this decomposition is unknown.

A sealed tube pyrolysis experiment was performed in order to pin down the endothermic transition at 200°. Hydrogen (0.755 m mol.) was obtained when piperidinoalane (1.10 m mol.) was heated at 200° for 15 minutes in a sealed tube.

This is 90% of the calculated amount based on equation 7. The proton magnetic resonance spectrum of the benzene soluble pyrolysate was found to be identical with that of authentic bis(piperidino)alane. These data are taken as verification of the proposed (equation 7) pyrolysis.

The conversion of dialkylaminoalanes to the corresponding bis(dialkylamino)-alane (equation 7) appears to be a perfectly general reaction as evidenced by our DTA-TGA studies of the pyrolysis of diethylamino- and pyrrolidinoalane (Table III).

[Place Table III here.]

The DTA trace of diethylaminoalane showed thermal effects at 30, 180, and 240° (Table III). These effects are assigned to melting of the starting material, thermal decomposition according to equation 7, and decomposition of bis(diethylamino)alane respectively. Verification of the assignment of the effect occurring at 240° was obtained from DTA-TGA analysis of bis(diethylamino)alane which showed a similar endotherm at 240°. The weight loss accompanying the effect occurring at 180° was always greater than that predicted on the basis of equation 7. This is due to extraneous weight loss due to excessive "bumping" of the material. This could be diminished but not stopped by heating at a slower rate with a crucible cover. Quantitative characterization of this reaction was obtained by heating diethylaminoalane in an evacuated, sealed tube at 180° followed by analysis for hydrogen. Hydrogen (0.965 m mol.) was obtained from 1.52 m mol. of diethylaminoalane under these conditions. This is 90% of the calculated amount based on equation 7. Pyrrolidinoalane decomposes in an analogous fashion. Three endothermic effects (Table III) at 90, 150, and 305°C were observed. These are assigned to melting of the reagent, decomposition

Table III. Thermal Properties of Aminoalanes as Determined By DTA-TGA Analysis.

Compound	Temp. of DTA effect (endotherm)	Assignment
H_2AlNEt_2	30	melting
	180	formation of $HAl(NEt_2)_2$ + Al + H_2
	240	decom. of $HAl(NEt_2)_2$
$HAl(NEt_2)_2$	240	decom. of $HAl(NEt_2)_2$
$H_2AlNC_4H_8$	90	melting
	150	formation of $HAl(NC_4H_8)_2$ + Al + H_2
	305	decom. of $HAl(NC_4H_8)_2$
$HAl(NC_4H_8)_2$	300	decom. of $HAl(NC_4H_8)_2$
$H_2AlNC_5H_{10}$	60	melting
	195	formation of $HAl(NC_5H_{10})_2$, Al and H_2
	310	decom. of $HAl(NC_5H_{10})_2$
$HAl(NC_5H_{10})_2$	100	melting
	310	decom. of $HAl(NC_5H_{10})_2$

according to equation 7, and decomposition of bis(pyrrolidino)alane respectively. Bis(pyrrolidino)alane exhibited a similar decomposition endotherm at 300°C.

These pyrolyses confirm conclusions based on our studies of the direct preparation of aminoalanes and in particular on our inability to prepare the dialkylaminoalanes in high yield. Dialkylaminoalanes have been shown to decompose according to reaction 7 slowly by refluxing in hydrocarbon solvent and rapidly by heating the neat material at the decomposition temperature.

The exact nature of the thermal decomposition of bis(dialkylamino)alanes could not be determined by these DTA-TGA studies due to bumping in the crucible at the decomposition temperatures. This could not be stopped by heating at slow rates with a crucible cover. Possible modes of decomposition include 1) formation of the corresponding tris(dialkylamino)alane, aluminum and hydrogen (equation 8) or 2) olefin elimination and formation of the corresponding alazine, and alkylamine (equation 9).

$$3\ HAl(NR_2)_2 \rightarrow 2\ Al(NR_2)_3 + Al\downarrow + 3/2\ H_2\uparrow \qquad (8)$$

$$3\ HAl(N(CH_2CH_2R)_2)_2 \rightarrow [HAlNR]_3 + 3\ H_2NR + 6\ CH_2{=}\overset{H}{\underset{|}{C}}{-}R\uparrow \qquad (9)$$

Reaction 8 is an extension of the process observed in reaction 7 while reaction 9 is predicted on the basis of reports concerning the pyrolysis of bis(dialkylamino)boranes.[12] The latter studies indicated that pyrolysis of bis(dialkylamino)-

(12) H. Steinberg and R. J. Brotherton, "Organoboron Chemistry," John Wiley and Sons, New York, N. Y., Volume II (1966) p. 4.

boranes result in the formation of the corresponding borazine and mono alkylamine. These reactions were not characterized quantitatively however. Additional work is required in order to characterize the bis(dialkylamino)alane pyrolysis. These studies would most logically involve DTA-TGA studies (in a hermetically sealed crucible) and sealed tube pyrolyses followed by quantitative determination of reaction products (using a vacuum line manifold to separate and analyze volatile components).

Spectroscopic Studies of Amino Alanes - Aminoalanes form self-associated species in hydrocarbon solution. Dialkylaminoalanes are trimeric in benzene while corresponding bis(dialkylamino)alanes are mainly dimeric[3] (Table 5). Lesser association in the latter compounds is undoubtedly a result of (1) greater steric crowding in the more highly substituted alane derivatives and (2) lessening of aluminum acidity as a result of aluminum-nitrogen bonding. Tris(dimethylamino) alane is the only known tris-aminoalane which is associated in benzene, that being as a dimer. Aminoalanes could conceivably associate with formation of NR_2^- or H^- bridges; the latter is improbable since dimerization through coordinatively bonded amino groups is favored over an Al-H-Al three-centered bridge bond. The most logical structures for the amino alanes based on these general considerations are Structures I, II and III (Page 53). In addition, these structures are consistent with those which were demonstrated for homologous aminoboranes[13] and proposed for alkoxy alanes[14] on the basis of X-ray, nmr,

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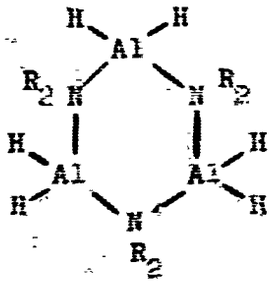
(13) L. K. Trefonas and W. N. Lipscomb, J. Am. Chem. Soc., 81, 4435 (1959).

(14) H. Nöth and H. Suchy, Z. Anorg. Allg. Chem. 358 (1-2), 44 (1968).

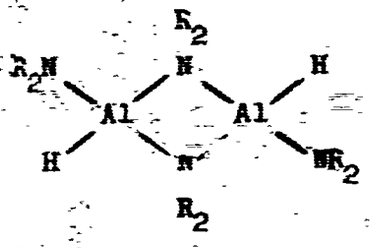
Dialkylaminoalane

Structure I



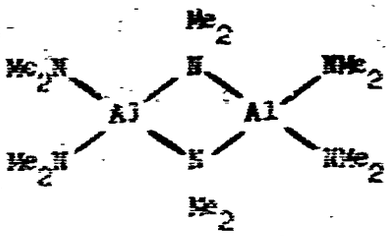
Bis(dialkylamino)alane

Structure II



Tris(dimethylamino)alane

Structure III



infrared and dipole moment studies.

The expected range for the Al-H stretching vibration[15] is 1600-1900 cm^{-1},

(15) H. M. Alpatova, T. N. Dymova, Yu. M. Kessler, and Om. K. Osipov, Russ. Chem. Rev., 37, 99 (1968).

with a bridging hydride showing a relatively broad band around 1600 cm^{-1}. An increase in coordination on the aluminum atom normally shifts the Al-H bands to smaller wave numbers. Substitution of hydride hydrogen atoms by electronegative substituents strengthens the Al-H bond as a consequence of inductive effects.

The Al-H stretching valence vibration for the dialkylaminoalanes (neat or in solution) occurs at ~1830 cm^{-1} (Table IV).

[Place Table IV here.]

The Al-H deformation frequencies ranged from 725 to 735 cm^{-1}. The position of these bands suggests a four-valent aluminum with hydrogen atoms bonded in terminal positions, in support of the amino bridged structure (I). The proton magnetic resonance spectral data also are in support of this structure. The dialkylaminoalanes exhibited only one kind of hydridic hydrogen and dialkylamino environment (Table V). The proton magnetic resonance spectrum of piperidinoalane is shown

[Place Table V here.]

in Figure III. The signals at 5.76 (singlet) 7.13 (triplet) and 8.63 τ (multiplet) of relative intensities 1.0:2.1:3.2 are assigned to hydridic hydrogen, bridging nitrogen α methylene and superisposition of bridging nitrogen β and γ methylene respectively. It occurred to us that the hydride resonance appears at an abnormally low chemical shift for a main group metal hydride; however, the

Table IV. Infrared Spectral Data of Aminoalanes

Compound	Al-H str. frequency	Al-H deformation frequency
$HAl(NMe_2)_2$	1824	——
H_2AlNEt_2	1829	734
$HAl(NEt_2)_2$	1832	692
$H_2AlNC_4H_8$	1832	729
$HAl(NC_4H_8)_2$	1824	695
$H_2AlNC_5H_{10}$	1828	725
$HAl(NC_5H_{10})_2$	1825	688

Table V Aminoalane Proton Magnetic Resonance Spectral Parameters.

Compound	Solvent	$i^{3,5}$	τ	Multiplicity	Rel. Area	Assignment
$HAl(NMe_2)_2$	Benzene	2.4	6.17	singlet	1.0	Al-H
			7.19	"	6.0	Terminal dimethylamino
			7.67	"	6.0	Bridging dimethylamino
$Al(NMe_2)_3$	"	[illegible]	[illegible]	"	2.0	Terminal dimethylamino
			7.51	"	1.0	Bridging dimethyamino
$H_2AlNC_5H_{10}$	"	3.6	5.76	singlet	1.0	Al-H
			7.13	triplet	1.1	Bridging nitrogen α methylene
			8.63	multiplet	3.2	Bridging nitrogen β and γ methylene
$HAl(NC_5H_{10})_2$	"	2.2	6.80	triplet	1.0	Terminal nitrogen α methylene
			7.10	triplet	2.0	Bridging nitrogen α methylene
			8.43	multiplet	3.0	Superimposition of terminal and bridging nitrogen β and γ methylene
$H_2AlNC_4H_8$	"	3	6.79	triplet	1.0	Bridging nitrogen α methylene
			8.32	triplet	1.0	Bridging nitrogen β methylene
$HAl(NC_4H_8)_2$	"	2	6.69	triplet	1.0	Terminal nitrogen α methylene
			6.99	triplet	1.0	Bridging nitrogen α methylene
			8.29	multiplet	2.0	Terminal and bridging nitrogen β methylene
$HAl(NEt_2)_2$	"	?		multiplet	2.0	See Figure V
				multiplet	3.0	
H_3AlNMe_3	"	2.3	5.80	singlet	1.0	Al-H
			7.96	singlet	3.0	trimethylamine

compounds R_2AlH[16] and H_3AlNMe_3 were found to exhibit hydride signals at

(16) E. G. Hoffmann, Z. Anal. Chem., 170, 177 (1959).

6.3 and 5.8 τ respectively. Proton magnetic resonance spectra of the remaining dialkylaminoalanes (Table V) are also consistent with structure I, although a hydride resonance was not observed for all of these. This is attributed to a result of the relatively large electric quadrupole moment of Al^{27} and coupling with the unsymmetrical field.

The Al-H stretching frequencies of the bis(dialkylamino)alanes (neat or in solution) occur in the range 1822 to 1830 cm^{-1} (Table IV). These are again indicative of four coordinate aluminum atoms with hydrogen bonded in terminal positions, in accord with structure II. The proton magnetic resonance spectra of the bis(dialkylamino)alanes showed only one hydridic environment (when this could be observed) and two nonequivalent dialkylamino environments of equal intensity. These data are also consistent with structure II. Specifically, bis(dimethylamino)alane exhibited proton signals at 6.17, 7.19, and 7.67 τ of relative areas 1.6:6.0:6.0 (Figure IV). These are assigned to hydridic hydrogen, terminal, and bridging dimethylamino environments respectively. The dimethylamino resonances were assigned by reference to the spectrum of dimeric tris-(dimethylamino)alane (Figure IV) in benzene which shows terminal and bridging amino signals at 7.23 and 7.51 τ respectively (relative area ratios 2.0:1.0 respectively). The spectral assignment for bis(piperidino)alane is a bit more complex owing to the presence of β and γ methylene in addition to α nitrogen methylene environments. The spectrum of this compound in benzene solution

consisted of signals at 6.80 (triplet), 7.10 (triplet) and 8.43 τ (complex mult plet) of relative areas 1.0:1.0:3.0 respectively (Figure III). These are assigned to terminal nitrogen α methylene, bridging nitrogen α methylene and superimposition of both terminal and bridging nitrogen β and γ methylene protons respectively. Resonance of the hydridic proton was not observed. These data indicate that bridging and terminal dialkylamino nonequivalence (of structure II) is experienced most drastically by methylene groups bonded α to the nitrogen and less by methylene groups bonded β and γ.

The proton magnetic resonance spectrum of bis(diethylamino)alane was the most complex and requires detailed explanation (Figure V). The spectrum is consistent with a dimer of structure II but is complicated by fortuitous overlap of bridging and terminal nitrogen methylene quartets and methyl triplets. Two fairly distinct methylene quartets of approximately equal area are resolved; however, the signals for the methyl groups appear as a 1:4:4:1 quartet. This is assigned to overlapping of both the central and high field components of one methyl triplet with the central and low field components of the other. A 1:4:4:1 quartet is predicted if the two triplet signals which overlap are each present in equal intensity.

In summary this work provides a reasonably detailed study of the direct synthesis of aminoalane compounds by the reaction of aluminum, hydrogen and secondary amines. Although bis and tris(dialkylamino)alanes were synthesized in high yields, dialkylaminoalanes could be prepared only in modest yield due to the thermal instability of these compounds.

Spectroscopic data (infrared and proton nmr) were compiled for these compounds and used to (1) characterize reaction products (2) monitor pyrolysis reactions and (3) provide structural information.

Figure I. Proton Magnetic Resonance Spectral Study of the Pyrolysis of $H_2AlNC_5H_{10}$ in Boiling Toluene. Spectra were recorded in benzene solution: A, t = 0 spectrum of piperidinoalane; B, spectrum obtained after heating for 2.5 days; C, after heating for 6.5 days; D, after heating for 8.5 days.

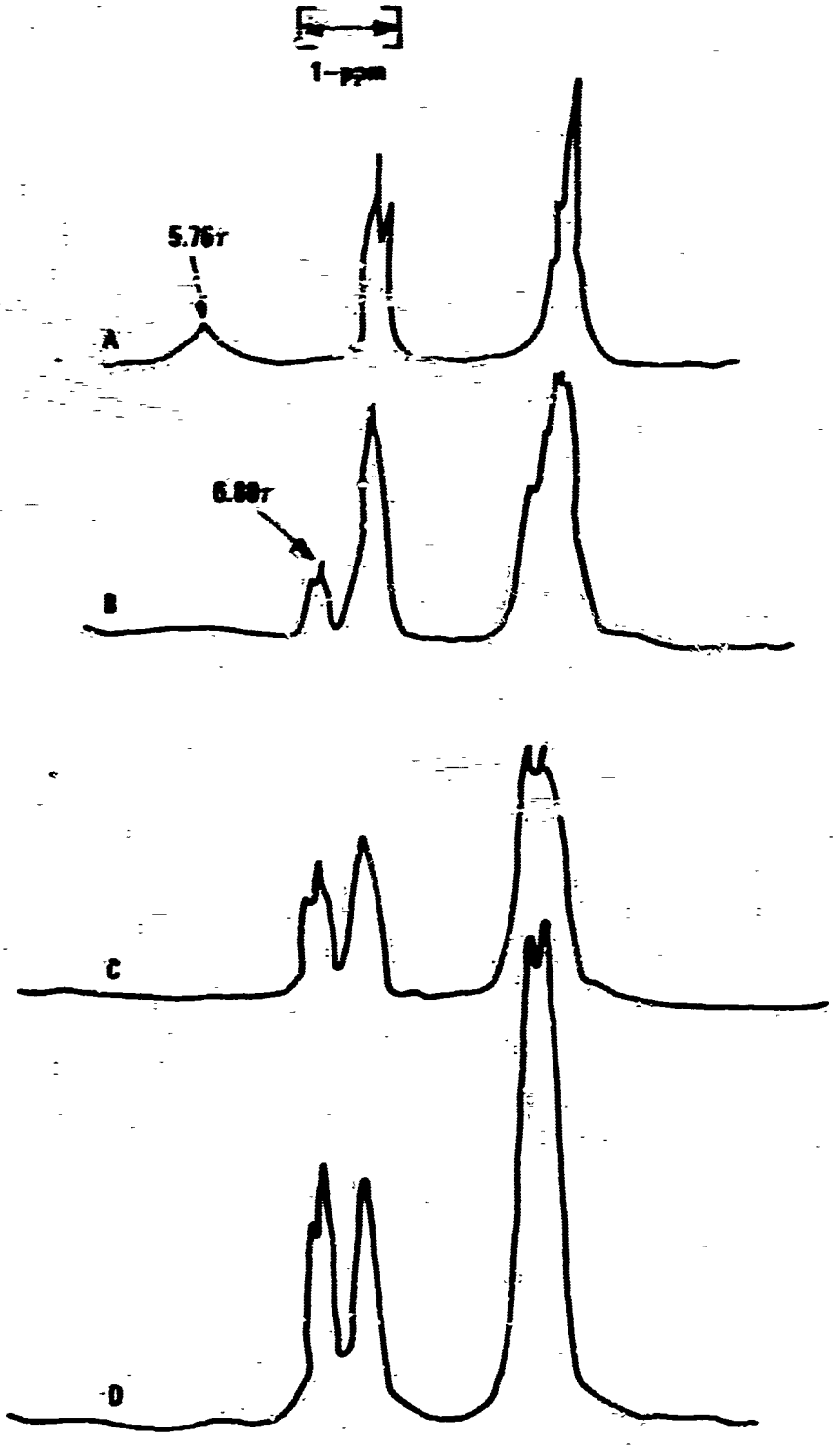

1-ppm
5.76τ
A
6.88τ
B
C
D

Figure II. DTA-TGA traces of $H_2AlNC_5H_{10}$ and $HAl(NC_5H_{10})_2$. A and B are DTA and TGA traces for $H_2AlNC_5H_{10}$ (sample size 53.0 M gr.) respectively; C and D are DTA and TGA traces for $HAl(NC_5H_{10})_2$ (55.7 M gr.) respectively.

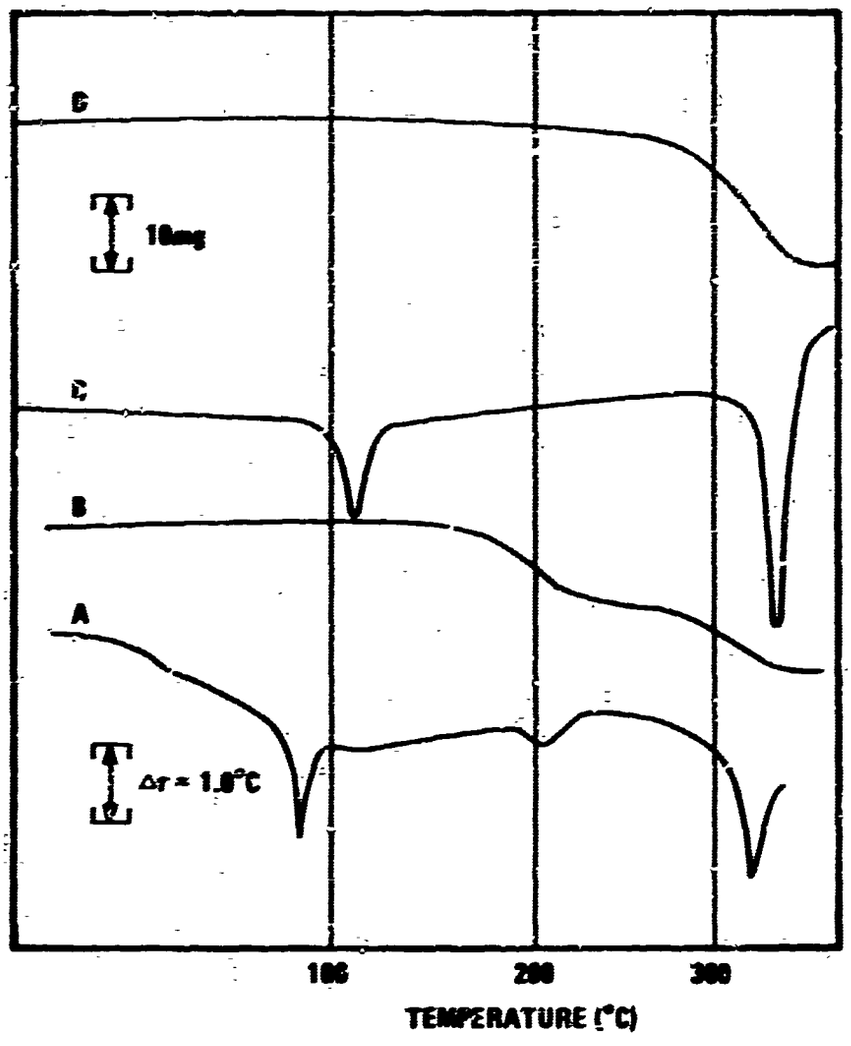

C
10mg
B
A
ΔT = 1.0°C
100
200
300
TEMPERATURE (°C)

Figure III. Representative Proton [illegible] of bis(piperidino)alane in Benz[illegible]

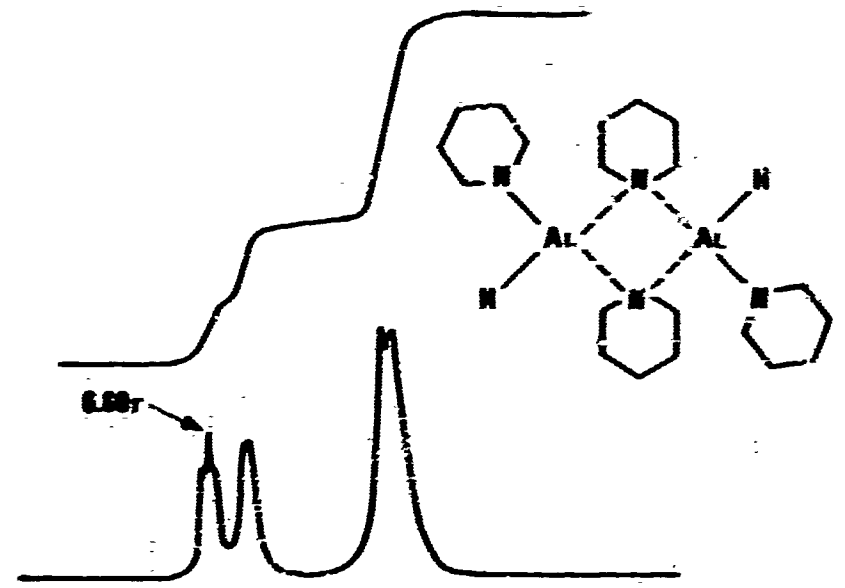
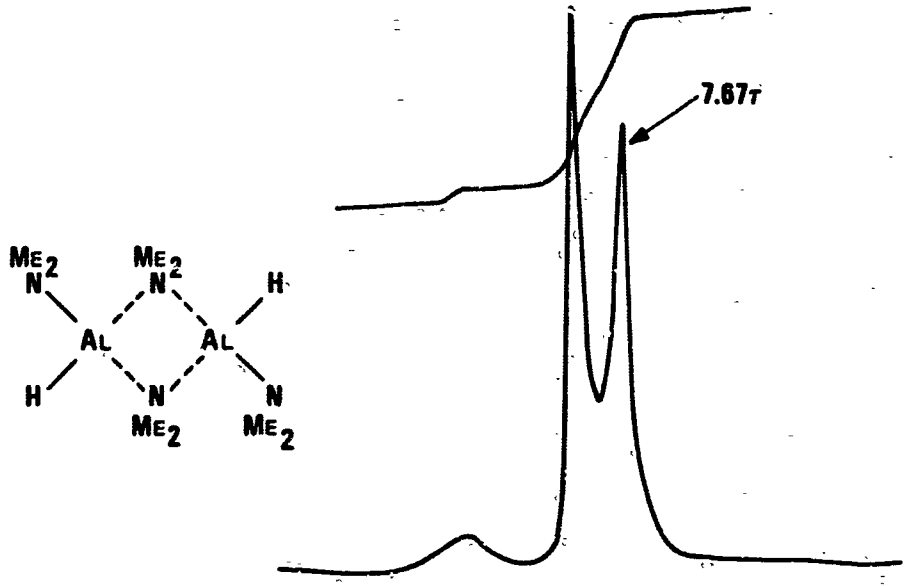
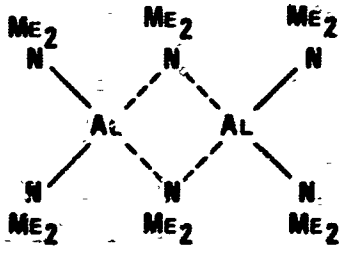
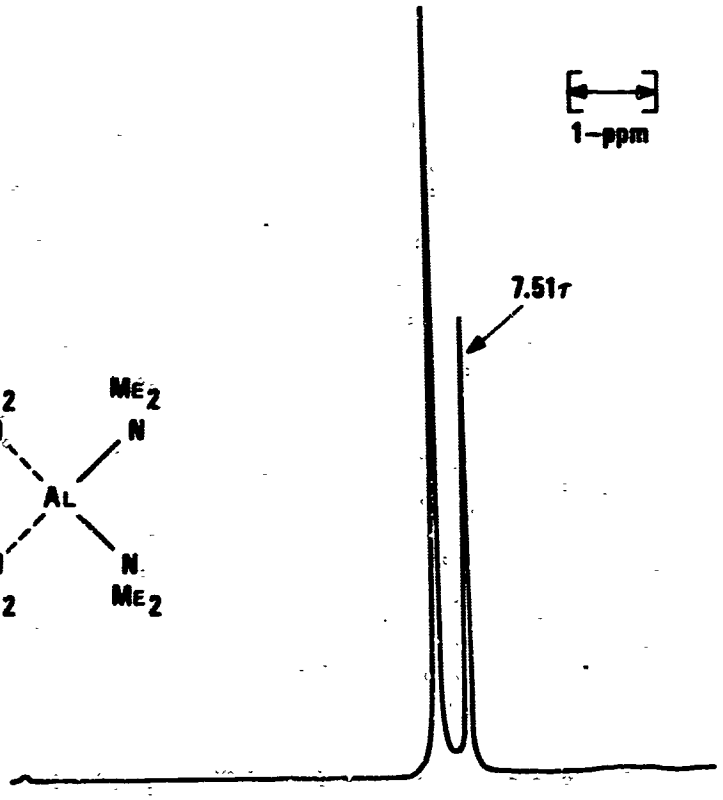

6.00τ
1 ppm
5.76τ

Figure IV. Proton Magnetic Resonance Spectra of bis- and tris(dimethylamino)-alane in Benzene Solution.

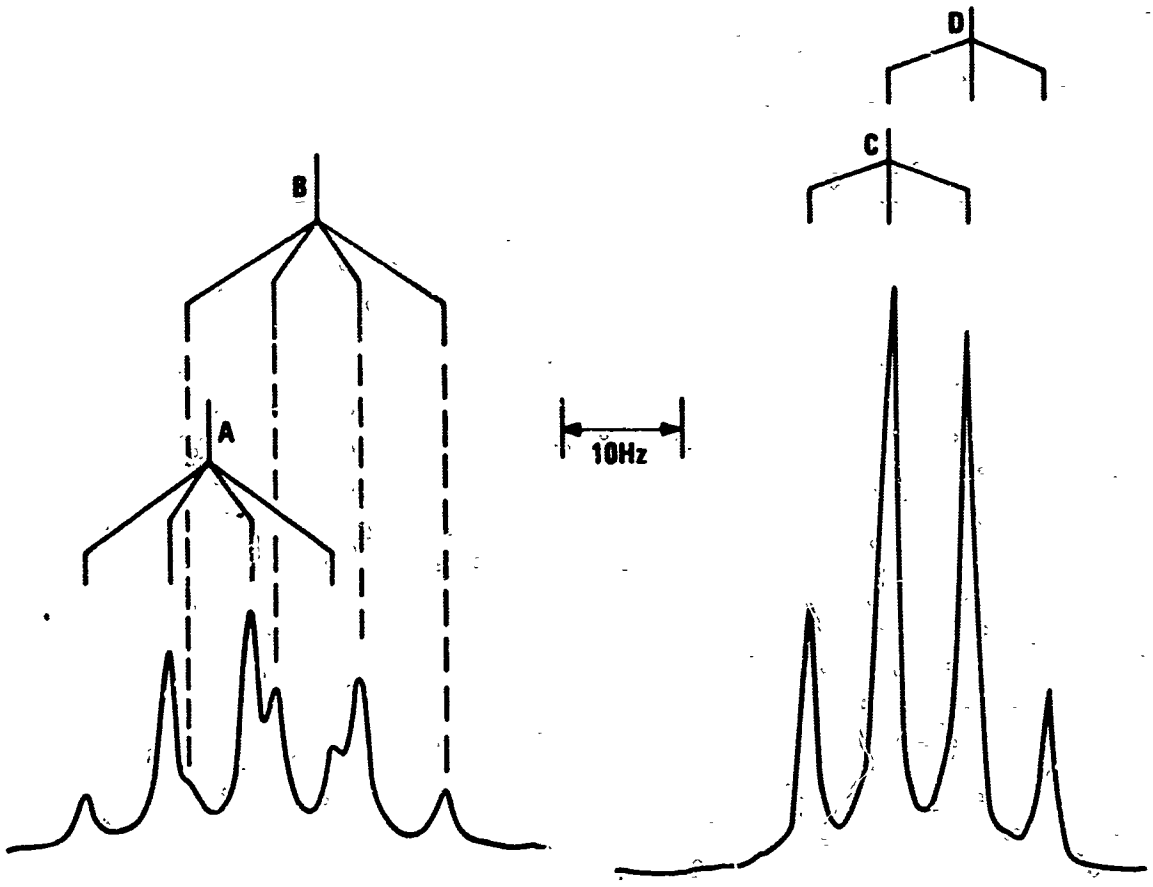

7.67τ


Me2
N
Al
H
Me2


1-ppm
7.51τ

Me2
N
Al
Me2

Figure V. Expanded scale Proton Magnetic Resonance Spectrum of Bis(diethylamino)-alane in Benzene Solution: A, Methylene Quartet at 6.80 τ; B, Methylene Quartet at 6.93 τ; C, Methyl Triplet at 8.77 τ; D, Methyl Triplet at 8.91 τ.


D
C
B
A
10Hz

The Direct Synthesis of Aminoboranes

Roger A. Kovar, R. Culbertson, and E. C. Ashby

Abstract

Detailed studies of the synthesis of aminoboranes by the direct reaction of aluminum, hydrogen, diethylamine, and triphenylborate under mild conditions are reported. The exact products which are prepared have been shown to be a function of the phenylborate-diethylamine ratio Tris(diethylamino)borane (81%) is prepared in admixture with bis(diethylamino)borane (5%) when diethylamine is used as solvent. Bis(diethylamino)borane is prepared exclusively and in high yield (80%) by aluminum-hydrogen reduction of phenylborate and diethylamine in a molar ratio of 1:2 in benzene solvent. Aluminum-hydrogen reductions of equivalent molar quantities of phenylborate and diethylamine in benzene did not afford high yields of the expected diethylaminoborane. Instead, nearly equivalent molar quantities of $HB(OPh)NEt_2$ and $B(OPh)_2NEt_2$ were isolated. This reaction was found to be insensitive to changes in reaction time or temperature. The reaction sequence which is proposed to explain formation of the latter products involves (1) intermediate formation of AlH_3 (equation 1), (2) reaction between AlH_3 and diethylamine forming the more thermodynamically stable bis(diethylamino)-alane (equation 2), and (3) reduction of phenylborate by bis(diethylamino)alane (equation 3).

$$Al + 3/2\ H_2 \rightarrow AlH_3 \qquad (1)$$

$$AlH_3 + HNEt_2 \rightarrow AlH_3 \cdot NEt_2H \xrightarrow{-H_2} H_2AlNEt_2 \xrightarrow[-H_2]{HNEt_2} HAl(NEt_2)_2 \qquad (2)$$

$$2\ B(OPh)_3 + HAl(NEt_2)_2 \rightarrow HB(OPh)NEt_2 + B(OPh)_2NEt_2 + Al(OPh)_3 \qquad (3)$$

This sequence was verified by independent studies of the exchange reaction between bis(diethylamino)alane and 1 and 2 equivalents of phenylborate.

Introduction

The use of aminoborane compounds as catalysts,[1] reducing agents,[2] and as synthetic intermediates[3] has been reported, however more widespread use of these compounds is limited by the inconvenience of preparation and high cost of these reagents. Until now aminoboranes have been prepared by the reaction of diborane with secondary amines[4] or of an alkali metal borohydride with a dialkylammonium chloride.[5]

(1) J. Derning and R. J. Sampson, Ger. Pat. 1,118,200 (1961, to Imperial Chemical Industries, Lt.).

(2) B. M. Mikhailov and V. A. Dorakhov, Proc. Acad. Sci., USSR, Chem. Sect. (Eng. Transl.), 136, 51 (1961).

(3) H. Steinberg and R. J. Brotherton, "Organoboron Chemistry," John Wiley and Sons, Inc., New York, N. Y., Volume 2 (1966).

(4) H. Nöth and E. Beyer, Chemische. Ber. 93, 938 (1960).

(5) G. W. Schaeffer and E. R. Anderson, J. Am. Chem. Soc., 71, 2143 (1949).

$$B_2H_6 + 2\ HNR_2 \rightarrow 2\ H_3BNR_2H \xrightarrow{-H_2} H_2BNR_2 \qquad (4)$$

$$NaBH_4 + R_2NH_2^+Cl^- \rightarrow H_3BNR_2H + NaCl + H_2 \xrightarrow{-H_2} H_2BNR_2 \qquad (5)$$

We wish to report the convenient and economical synthesis of aminoboranes in high yield by aluminum-hydrogen reduction of phenylborate in the presence of secondary amines at moderate temperature and pressure. The aluminum-hydrogen reducing system has been shown to function successfully in the reduction of boric oxide to diborane in 40-50% yield at 750 atm., in the presence of aluminum chloride[6] (equation 6) and in the reduction of phenylborate (in the presence of tertiary amines) to form amine boranes in nearly quantitative yield (equation 7).[7]

(6) T. A. Ford, G. H. Kalb, A. L. McClelland and E. L. Multerties, Inorg. Chem., 3, 1032 (1964).

(7) E. C. Ashby and Walter E. Foster, J. Am. Chem. Soc., 84, 3407 (1962).

$$6(AlH_xCl_{3-x}) + xB_2C_3 \rightarrow xB_2H_6 + 6\ AlO_{x/2}Cl_{3-x} \qquad (6)$$

$$3/2\ H_2 + NR_3 + Al \rightarrow H_2BNR_3 + Al(OPh)_3 \qquad (7)$$

The amine boranes are easily separated from the by-product triphenoxyaluminum by filtration, triphenoxyaluminum being insoluble in hydrocarbon solvents. This reaction was thought to proceed through the intermediate formation of AlH_3 followed by reduction of the phenylborate to "BH_3" and the reaction of "BH_3"

with the tertiary amine. Reaction of aluminum, hydrogen, and equal molar mixtures of phenylborate and secondary amines at low temperatures was predicted in an analogous way to generate the secondary amine boranes (these are stable only at low temperature) (equation 8) while reaction of phenylborate and

$$B(O\phi)_3 + Al + 3/2\ H_2 + HNR_2 \xrightarrow{100\text{-}150^\circ} H_3B{:}NR_2 + Al(O\phi)_3 \qquad (8)$$

secondary amines in 1:1, 1:2 and 1:3 stoichiometry at high temperatures was predicted to generate the aminoboranes $H_nB(NR_2)_{3-n}$ (equation 9).[8]

(8) R. E. McCoy and S. H. Bauer, J. Am. Chem. Soc., 78, 2061 (1956).

$$H_3BNR_2 \xrightarrow[-H_2]{} H_2BNR_2 \xrightarrow[-H_2]{HNR_2} HB(NR_2)_2 \xrightarrow[-H_2]{HNR_2} B(NR_2)_3 \qquad (9)$$

Thus, the direct synthesis of a variety of amine and amino borane compounds depending on the initial stoichiometry of the reactants and on the reaction temperature were predicted. The economics of these processes are worthy of note since the raw materials are borax, aluminum, and hydrogen. The final products are amine- or aminoboranes and triphenoxyaluminum which can be hydrolyzed in the presence of sulfuric acid to regenerate phenol and form alum ($Al_2SO_4)_3$). The regenerated phenol can then react with borax and H_2SO_4 to form phenyl borate and the aluminum values are utilized as alum, a seizing material used in the paper industry.

$$(PhO)_3B + Al + H_2 \xrightarrow{H_nNR_{3-n}} H_3BNH_nR_{3-n} + Al(OPh)_3 \qquad (10)$$

$$\text{Borax} + H_2SO_4 \rightarrow PhOH + Al_2(SO_4)_3 \text{ (alum)}$$

$$Al(OPh)_3 + H_2SO_4 \rightarrow Al_2(SO_4)_3 \text{ (alum)}$$

The present study was undertaken to establish procedures for preparing exclusively, in high yield, each of the predicted reaction products. Description of the course of the aluminum-hydrogen phenylborate reduction was of additional interest and several experiments were conducted to describe the reaction sequence involved.

Experimental

Equipment and Materials. - Manipulation of air sensitive materials was accomplished by use of standard bench top techniques and dry nitrogen purge or a dry box equipped with atmosphere purification system for removal of oxygen and moisture. Infrared spectral measurements were obtained using a Perkin Elmer 621 Automatic Grating Spectrophotometer. Samples were prepared for analysis in the dry box. Spectra of liquid samples were obtained from analysis of the neat material between KBr salt plates while spectra of solid samples were obtained as the Nujol mull. Proton magnetic resonance spectra were obtained using a Varian A-60 magnetic resonance instrument using solvent signals (either benzene or methylenedichloride) as internal standard.

Hydrogenation reactions were performed using a 300 ml. Magnedrive Autoclave Unit from Autoclave Engineers Inc. The chamber was usually charged in the dry box, and contents heated with stirring under hydrogen for a predetermined time. After

sufficient cooling the chamber was vented and soluble products filtered from excess unreacted aluminum and triphenoxyaluminum in the dry box.

Benzene used as the solvent in the hydrogenation reactions was purchased from Fisher Chemical Co. (Certified ACS Grade) and distilled from $NaAlH_4$ prior to use. Diethylamine was purchased from Eastman Chemicals and distilled onto active molecular sieve type 4-A. Aluminum powder (600 mesh) was obtained from the Alcan Aluminum Corp. The aluminum was "activated" prior to use by the Ziegler activation process.[9] Boric acid and phenol, used to prepare phenylborate,[10] were

(9) E. C. Ashby, G. J. Brendel and H. E. Redmon, Inorg. Chem., 2, 499 (1963).

(10) T. Colclough, W. Gerrard, and M. F. Lappert, J. Chem. Soc., 907 (1955).

obtained from Fisher Chemical and used without further purification. Ultra Pure Hydrogen (99.9995%) was obtained from the Matheson Corp. and used without further purification.

Analyses. - Aminoboranes are relatively stable toward hydrolysis.[11] Complete

(11) E. Wiberg, A. Bolz, and P. Bucheit, Z. Anorg. Allgem. Chem., 256, 285 (1948).

hydrolysis was effected by boiling in water for extended periods (several hours). Samples for analysis were weighed in 50-100 ml. flasks, attached to a distillation column, and 50 ml. distilled water added. The mixtures were heated to distill the evolved amine and water into a receiver kept cold with a water-ice slurry. Nitrogen in the distillate was determined by titration with standard acid. Boron was determined by standard base titration of the boric acid mannitol complex.[12]

(12) R. D. Strahm and M. F. Hawthorne, Anal. Chem., 33, [illegible]

The unsymmetrical phenoxydiethylaminoborane ($HB(O\phi)NEt_2$) was analyzed by a modification of the above procedure. Boron was separated from phenol (after hydrolysis and removal of the amine by distillation) by distillation of boron as the methyl borate ester.[13] Boron was analyzed in the distillate as described above.

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(13) H. Steinberg, "Organoboron Chemistry," John Wiley and Sons, Inc., New York, N. Y., I, 38 (1964).

Hydrogen in these compounds was not measured analytically owing to the difficulty of effecting complete hydrolysis on a hydrogen gas liberation manifold. The presence of hydrogen (or absence) was determined qualitatively by infrared spectral techniques.

Reactions: Aluminum-Hydrogen Reductions of Phenylborate

A. Direct Preparation of $HB(NEt_2)_2$. - In a typical experiment phenylborate (30 gr. or 0.1 mol.), diethylamine (0.2 mol.), aluminum metal (5 gr. or 1.5 mol.), and benzene (100 ml.) were heated at 180°C under 3000 psig hydrogen for 5 hr. Vacuum distillation (after filtration of the reaction mixture to remove unreacted aluminum metal and triphenoxyaluminum and removal of benzene solvent under vacuum) gave a single fraction which boiled at 62° and 15.0 mm. Yield was 13.3 gr $HB(NEt_2)_2$ or 85%. Anal. Calc. for $HB(NEt_2)_2$: B, 6.94; N (as amine), 92.5. Found: B, 6.82; N, 91.3. Triphenoxyaluminum (~ 15 gram) (determined by comparison of infrared spectral data) was left in the distillation flask.

B. Direct Preparation of $B(NEt_2)_3$. - Phenylborate (0.1 mol.) aluminum metal (2.7 gr or 0.1 mol.) and diethylamine (as solvent 100 ml.) were heated at 180°C under 3000 psig hydrogen for 24 hr. Vacuum distillation (after filtration and removal of solvent under vacuum) gave two fractions. Bis(diethylamino)borane

at 63° and 15 mm (yield 19%) and tris(diethylamino)boron at 95° and 11 mm (71% yield). Anal. Calc. for $B(NEt_2)_3$: B, 6.94; N (as amine), 92.5. Found: B, 6.82; N, 91.3.

C. Attempted Direct Preparation of $H_2B(NEt_2)$. - Phenylborate (0.1 mol.), diethylamine (0.1 mol.), aluminum metal (5 gr. or 0.15 mol.), and benzene (100 ml.) were heated at 180° under 3000 psi hydrogen for 2 hr. (equation 9, Table II). Vacuum distillation (after filtration and removal of solvent under vacuum) gave two fractions. The first fraction ($HB(O\phi)NEt_2$) distilled at 90° and 5 mm while the second fraction ($B(O\phi)_2NEt_2$) distilled at 120° and 0.5 mm. Anal. Calc. for $HB(O\phi)NEt_2$: B, 6.11; N (as amine), 40.6. Found: B, 6.12, N, 40.2. Infrared spectral analysis indicated both aromatic, N-alkyl, and active hydride environments (B-H at 2498 cm^{-1}). Proton magnetic resonance spectroscopic analysis (in CH_2Cl_2) showed signals at 2.87 τ (aromatic Multiplet), 6.76 τ (Ethyl methylene quartet) and 8.80 τ (Ethyl methyl triplet) of relative areas 4.7:4.0:6.2 respectively. Anal. Calc. for $B(O\phi)_2NEt_2$: B, 4.02, N (as amine), 26.8. Found: B, 3.82; N, 25.6. Infrared spectral analysis indicated the absence of a B-H stretching bond and the presence of both aromatic and N-alkyl environments. The proton magnetic resonance spectrum of this compound in CH_2Cl_2 consisted of signals at 3.07 τ (aromatic multiplet) 6.86 τ (Ethyl methylene quartet) and 8.86 τ (Ethyl methyl triplet) of relative areas 10.0:3.7:6.2 respectively.

Essentially the same results were observed when the reaction time was extended to 4 and 24 hours (Reactions 4 and 5, Table II) with the exception that in each case a small quantity (< 1% yield) of $H_2B(NEt_2)$ was vapor transferred (at 70° and 0.25 mm) into a Schlenk tube cooled in a dry ice acetone slurry prior to vacuum distillation of the major components as described above. Anal. Calc. for

$H_2B(NEt_2)$: B, 12.72; N (as amine), 87.3. Found: B, 12.8; N, 88.2. The infrared spectrum of this material (Nujol mull) was identical to that of $H_2B(NEt_2)$ prepared by unequivocal synthesis (Vide infra). The observed melting point of 44° corresponds to the literature[14] value of 44°.

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(14) H. I. Schlesinger, H. C. Brown, H. R. Hoekstra, and L. R. Rapp, J. Am. Chem. Soc., 75, 199 (1953).

Aminoalane-Phenylborate exchange reactions

A. Reaction of Equal Molar Quantities of Bis(diethylamino)alane and Phenylborate. - Phenylborate (2.89 gr. or 0.0100 mol.), and bis(diethylamino)-alane (1.707 gr. or 0.00995 mol.) prepared by the direct reaction of aluminum, hydrogen, and diethylamine[15] at 180° were weighed and mixed in the dry box.

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(15) E. C. Ashby and R. A. Kovar, (In Press).

Immediate evolution of heat was noted accompanied by solution of the phenylborate. The infrared spectrum (neat) was recorded and showed a B-H stretching frequency at 2500 cm^{-1} and no Al-H stretching bands. Benzene (25 ml.) was added and the reaction mixture stirred at 55° for 12 hr. A white precipitate (later identified as triphenoxyaluminum by comparison of infrared spectral data) had formed. The mixture was filtered, solvent removed under vacuum and product spearated by vacuum distillation. The product boiled at 63° and 15 mm and was identified as $HB(NEt_2)_2$ by comparison of infrared spectral data. Yield was 1.5 gr. or 96% recovery of boron. Some .8 gr. triphenoxyaluminum remained in the distillation flask.

B. Reaction of Phenylborate and a Half Molar Equivalent of Bis(diethylamino)alane. - Phenylborate (9.2 gr. or 0.0318 mol.) and bis(diethylamino)alane (2.74 gr. or 0.0159 mol) were mixed in 25 ml. benzene. Evolution of heat was noted. The mixture was stirred for 12 hr. at 55°. White solid (later identified as triphenoxyaluminum by infrared spectral comparison) formed during this period. The solution was filtered and solvent removed under vacuum. Vacuum distillation gave two products, $HB(O\phi)NEt_2$ at 90° and 5 mm (2.87 gr. or 0.0162 mol.) and $B(O\phi)_2NEt_2$ at 120° and 0.5 mm (2.69 gr or 0.0101 mol.). These products were identified by comparison of appropriate infrared spectral data. Some triphenoxyaluminum remained in the distillation flask. Triphenoxyaluminum obtained in both the filtration and distillation steps was combined and the yield found to be 5.629 gr. or 0.184 mol.

Unequivocal synthesis of $H_3B{\cdot}NEt_2$. - Diborane, generated by the reaction of $NaAlH_4$ and BF_3 in ether[16] was passed through a trap cooled in a dry-ice acetone slurry

(16) A. B. Burg and C. L. Randolph, J. Am. Chem. Soc., 71, 3451 (1949).

and allowed to bubble through diethylamine in benzene. Isolation of liquid $H_3B{\cdot}NEt_2$ was effected by removal of solvent under vacuum. Anal. Calc. based on $H_3B{\cdot}HNEt_2$: B, 12.4; N (as amine), 84. Found: B, 12.6; N, 85.6. Infrared spectral analysis revealed N-H and B-H stretching frequencies at 3260 and 2330 cm^{-1}, respectively.

Unequivocal synthesis of $H_2B{\cdot}NEt_2$. - Diethylaminoborane was prepared by pyrolyzing H_3BHNEt_2 at 200° for 4 hr. The crystalline product melted at 44° (literature[14] value 44°) and showed B-H stretching bands at 2422 and 2358 cm^{-1} and no N-H stretching band.

Results and Discussion

Pertinent data (reaction conditions, stoichiometries of reactants and reaction products) concerning aluminum-hydrogen reduction of phenylborate in the presence of diethylamine are summarized in Table I. Reference to this table indicates that attempts to prepare $B(NEt_2)_3$ and $HB(NEt_2)_2$ (reactions 1 and 2) respectively, were quite successful. In this connection bis(diethylamino)borane was prepared exclusively when two equivalents of diethylamine, phenylborate, aluminum and hydrogen were allowed to react. On the other hand, when diethylamine was used as solvent, tris(diethylamino)borane (81%) was generated in admixture with bis(diethylamino)borane (5%).

Attempts to prepare diethylaminoborane exclusively and in high yield were not successful. Product analysis of reaction 3 revealed the formation of two compounds, $HB(OPh)NEt_2$ in 42% yield and $B(OPh)_2NEt_2$ in 39% yield. Isolation of these products indicates incomplete reduction of the (B-OPh) bonds and suggests that aluminum-hydrogen reduction of phenylborate in the presence of equal equivalents of diethylamine involves a stepwise reduction of triphenylborate. These results suggest that additional time is required in order to effect complete reduction necessary for preparation of H_2BNEt_2. In this connection, reaction times were extended to 4 and 24 hr. (reactions 4 and 5). A low yield (< 1%) of H_2BNEt_2 was isolated in each of these reactions; however, the major products (and respective yields) were found to be identical, within experimental error, to results observed when the reaction time was 2 hr. The same products were isolated even when the reaction temperature was lowered to 100° (Reaction 6).

These data indicate that the aluminum-hydrogen reduction reaction is essentially complete after the first two hours of reaction and thus a particular

reaction sequence is suggested. Incomplete reduction of all phenoxyboron bonds suggests that (1) the active reducing agent is not an unlimited quantity of AlH_3 (generated by the reaction of excess Al and hydrogen) since AlH_3 would be expected to reduce phenylborate to BH_3 (2) the active reducing agent ("Al-H species") is present in limited quantity and functions only to reduce some of the phenylborate, and (3) the quantity of actual reducing agent is limited by the quantity of secondary amine present initially.

The reaction sequence which is consistent with these general requirements and which we propose is the sequence operative in these reactions involves (1) the intermediate formation of AlH_3 (by the reaction of aluminum and hydrogen (2) reaction of AlH_3 and diethylamine forming the more thermodynamically stable bis(diethylamino)alane and (3) reduction of phenylborate by the aminoalane. The exact sequence proposed is described below.

Step I:

$$2\ B(OPh)_3 + 2\ HNEt_2 + 2\ Al \xrightarrow{H_2} 2\ B(OPh)_3 + HAl(NEt_2)_2 \qquad (11)$$

Step II:

$$2\ B(OPh)_3 + HAl(NEt_2)_2 \rightarrow HB(OPh)NEt_2 + B(OPh)_2NEt_2 + Al(OPh)_3 \qquad (12)$$

Independent verification of this reaction sequence has been obtained. We have found[15] that reaction of aluminum (in excess), hydrogen, and diethylamine in benzene solvent results in predominant formation of the corresponding bis(dialkylamino)alane.

$$Al + 3/2\ H_2 \xrightarrow{HNEt_2} H_3AlNEt_2H \xrightarrow[-H_2]{} H_2AlNEt_2 \xrightarrow[-H_2]{HNEt_2} [HAlNEt_2]_2 \qquad (13)$$

Bis(dialkylamino)alanes are more stable thermally than the corresponding dialkylaminoalane (H_2AlNR_2) and thus, the former compounds are formed preferentially.

The reaction of alanes in general with borate esters (Step II of the proposed sequence) has been studied in some detail by other workers. These studies provide information concerning the reduction of borates with alane,[17] alkoxyalanes,[17] and alkali metal hydrides;[18] however, the reduction of borate esters with aminoalanes has not been studied in any detail. We attempted to characterize the aminoalane reduction of phenylborate at two different stoichiometries. In the first reaction, equal molar quantities of bis(diethylamino)alane and phenylborate were allowed to react. Isolation of bis(diethylamino)borane was quantitative indicating the following overall reaction:

(17) H. Nöth and H. Suchy, Z. Anorg. Allg. Chem. 358 (1-2), 49-68 (1968).

(18) H. I. Schlesinger and H. C. Brown, et. al., J. Am. Chem. Soc., 75, 186 (1953).

$$\begin{array}{ccc} B(OPh)_3 + HAl(NEt_2)_2 & \rightarrow & HB(NEt_2)_2 + Al(OPh)_3 \\ \downarrow & & \downarrow\uparrow \\ HB(OPh)_2 + Al(NEt_2)OPh & \rightleftharpoons & HB(OPh)NEt_2 + Al(OPh)_2NEt_2 \end{array} \qquad (14)$$

The infrared spectrum of the neat mixture obtained after initial mixing of the reagents exhibited a B-H stretching frequency at 2500 cm^{-1} and no Al-H stretching frequency. These data indicate that the first step of the exchange,

transfer of hydrogen from aluminum to boron occurs rapidly; however, the observation that triphenoxyaluminum is solubilized in benzene (see experimental section) may indicate that the intermediates actually present in this reaction are mixed, unsymmetrical amino-phenoxy compounds. Equilibrium between these species allows isolation of the most volatile component ($HB(NEt_2)_2$), and forces the reaction to completion. These results indicate that aminoalanes exchange both hydrogen and secondary amino groups with triphenylborate when the aminoalane is present in sufficient quantity.

The reaction of phenylborate and a half molar equivalent of bis(diethylamino)alane was studied to determine whether the incompletely exchanged boron species $HB(O\phi)NEt_2$ and $B(O\phi)_2NEt_2$ could be isolated when the aminoalane is present in limiting quantity. Infrared spectral analysis of the mixture obtained after initial mixing of the reagents indicated the absence of an Al-H stretching frequency and the presence of a B-H stretching band at 2500 cm^{-1}. Thus, the first step of the exchange, transfer of hydride from aluminum to boron, occurs rapidly. Isolation of $HB(OPh)NEt_2$, $B(OPh)_2NEt_2$, and $Al(OPh)_3$ was nearly quantitative according to the proposed exchange reactions shown below.

$$2\ B(OPh)_3 + HAl(NEt_2)_2 \rightleftharpoons HB(OPh)NEt_2 + B(OPh)_2NEt_2 + Al(OPh)_3 \quad (15)$$

$$\downarrow \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow\uparrow$$

$$HB(OPh)_2 + Al(NEt_2)_2OPh + B(OPh)_3 \rightleftharpoons HB(OPh)NEt_2 + Al(OPh)_2NEt_2 + B(OPh)_3$$

Apparent solubilization of triphenoxyaluminum in benzene is indicative of a complex equilibria involving unsymmetrical, incompletely exchanged species. As

before, the most volatile components (in this case $HB(O\phi)NEt_2$ and $B(O\phi)_2NEt_2$) are isolated by vacuum distillation and the equilibrium is driven in one particular direction.

The aminoalane-phenylborate exchange reactions are in complete agreement with our observations concerning the direct reaction of equal molar mixtures of triphenylborate and diethylamine, aluminum, and hydrogen. These exchange reactions successfully account for formation of the exact products (with analogous % yields) and in addition provide direct explanation of the apparent solubilization of triphenoxyaluminum in benzene. These reactions provide convincing evidence that reactions of equal molar quantities of phenylborate and diethylamine with aluminum and hydrogen proceed through intermediate formation of the bis(diethylamino)alane.

It should also be emphasized that aluminum-hydrogen reductions of phenylborate in the presence of two and three equivalents of diethylamine could also proceed through the corresponding aminoalane intermediates $HAl(NEt_2)$ and $Al(NEt_2)_3$ respectively. No distinction concerning the reaction sequence is possible in these cases since all of those proposed predict formation of the observed products.

In summary, this work has provided an in depth study of the aluminum-hydrogen reduction of phenylborate in admixture with various stoichiometric amounts of diethylamine under varying reaction conditions. Details concerning the direct preparation of $HB(NEt_2)_2$ and $B(NEt_2)_3$ in high yield were specified. Attempts to prepare $H_2B(NEt_2)$ in an analogous way were not successful. Detailed studies of the reaction of aluminum and hydrogen and equivalent mixtures of diethylamine and phenylborate have shown that equal molar mixtures of $HB(O\phi)NEt_2$

and $B(O\phi)_2NEt_2$ result rather than the desired H_2BNEt_2. This reaction has been shown to proceed through intermediate formation of the bis(diethylamino)-alane with phenylborate, followed by aminoalane reduction of the phenylborate.

This work will be extended to include a description of the reaction of aluminum, hydrogen, phenylborate, and two equivalents of a variety of secondary amines. These will include dimethyl-, di-i-propyl-, di-phenylamine as well as piperidine and pyrrolidine. The reaction of dimethylamine, pyrrolidine, and piperidine with aluminum and hydrogen (in the absence of phenylborate) has been shown to form the corresponding bis(dialkylamino)alane, while no reactions were observed in the corresponding reaction with di-i-propyl- and di-phenylamine. Based on these observations we predict that aluminum-hydrogen reductions of phenylborate in the presence of two equivalents of a secondary amine will lead to formation of the bis(dialkylamino)borane when the secondary amine is dimethyl-amine, pyrrolidine, and piperidine but may lead to more complex results when the secondary amine is di-i-propyl- and di-phenylamine since phenylborate reductions in these cases may <u>not</u> proceed through intermediate formation of the corresponding aminoalane.

Table I

Direct Preparation of Aminoboranes

$$B(OPh)_3 + HNEt_2 + Al \xrightarrow[H_2,\ 3{,}000\ psi]{\Delta} H_nB(NEt_2)_{3-n} + Al(OPh)_3$$

Reaction No.	Initial Molar Ratio $B(O\phi)_3$:$HNEt_2$	Time Hr.	Temp. °C	Product and % Yield	
1	1:∞ (amine solvent)	24	180	$B(NEt_2)_3$	81
				$HB(NEt_2)_2$	5
2*	1:2	5	180	$HB(NEt_2)_2$	85
3*	1:1	2	180	$HB(OPh)NEt_2$	42
				$B(NEt_2)(OPh)_2$	39
4	1:1	4	180	$H_2B(NEt_2)$	< 1
				$HB(OPh)(NEt_2)$	40
				$B(NEt_2)(OPh)_2$	35
5	1:1	24	180	$H_2B(NEt_2)$	< 1
				$HB(OPh)NEt_2$	38
				$B(NEt_2)(OPh)_2$	37
6	1:1	24	100	$HB(OPh)NEt_2$	38
				$B(NEt_2)(OPh)_2$	47

*These results are each representative of three runs under the specified conditions.

Concerning the Reaction of Lithium and Sodium Hydride with Magnesium Halides in Ether Solvents. A Convenient and Economic Route to Reactive Magnesium Hydride. A Potential Route to $M_nM'H_{2+n}$.

R. D. Schwartz and S. C. Ashby

Abstract

Magnesium hydride was prepared in quantitative yield by the reaction of sodium hydride and magnesium bromide in tetrahydrofuran and with magnesium iodide in diethyl ether. The sodium iodide by-product could be separated from the magnesium hydride by stirring the mixture in tetrahydrofuran. Commercially available lithium hydride was found not to react with magnesium halides in tetrahydrofuran at room temperature although some reaction was detected at reflux temperatures. Lithium hydride prepared from the hydrogenolysis of t-butyl lithium was found to react slowly with magnesium bromide and not at all with magnesium chloride in tetrahydrofuran. No complex of the type M_nMgH_{2+n} was detected using excess alkali metal hydride.

Introduction

There are three general methods for preparing magnesium hydride.[1]

(1) K. M. Mackay, "Hydrogen Compounds of the Metallic Elements," Wilmer Brothers Limited, Birkenhead, Cheshire, 1966, p. 39.

The equations used to represent these methods are shown below (Eqs. 1-3).

$$(C_2H_5)_2Mg \xrightarrow{175^\circ} MgH_2 + 2\ C_2H_4 \qquad (1)$$

$$LiAlH_4 + 2\ Mg(C_2H_5)_2 \rightarrow 2\ MgH_2 + LiAl(C_2H_5)_4 \qquad (2)$$

$$Mg + H_2 \xrightarrow[200\ atm]{570^\circ} MgH_2 \qquad (3)$$

The pyrolysis of diethyl magnesium to form magnesium hydride (Eq. 1) was reported by Wiberg and Bauer.[2] The preparation of magnesium hydride from lithium aluminum hydride and diethyl magnesium (Eq. 2) was first reported by Schlesinger et. al.[3] They found that the preparation of pure magnesium hydride depended on the proportions of the reactants, the order of addition and the concentration of the solution. However, recent work in this laboratory has shown that magnesium hydride is formed regardless of the order of addition or the concentration of the solution.[4]

(2) E. Wiberg and R. Bauer, Z. Naturforsch., 5b, 396 (1950).

(3) G. D. Barbaras, C. Dillard, A. E. Finholt, T. Warlik, K. E. Wilzbach and H. I. Schlesinger, J. Am. Chem. Soc., 73, 4585 (1951).

(4) E. C. Ashby and R. G. Beach, unpublished results.

The formation of magnesium hydride from the elements (Eq. 3) occurs at 570° and 200 atm. with magnesium iodide used as a catalyst. This method is obviously an economic one and the magnesium hydride prepared by this method is commercially available. Unfortunately MgH_2 prepared from the elements is quite

unreactive even to air and water. On the other hand, magnesium hydride prepared by the reactions represented by equations 1 and 2 reacts violently with water.[1] Thus the methods represented by equations 1 and 2 have been used for the preparation of MgH_2 when active material is required.

In 1951 Wiberg[5] reported the preparation of magnesium hydride by the

(5) E. Wiberg and R. Bauer, Z. Naturforsch. 6b, 171 (1951).

reaction of lithium hydride and magnesium chloride in diethyl ether. He also stated that if lithium hydride were used in excess that a complex of the form Li_nMgH_{2+n} might be formed although it could have been a physical mixture of lithium hydride and magnesium hydride. Very few details were given in this report and no subsequent report has appeared.

The reaction of alkali metal hydrides with magnesium halides in ether solvents could be a more convenient and economical route to reactive magnesium hydride than the methods now available, especially if the less expensive and commercially available NaH was found to react with magnesium halide. The ideal situation of course would be for sodium hydride to react with a magnesium halide that is soluble in some solvent to form MgH_2 which is insoluble in all solvents and the by-product sodium halide which would be soluble in the reaction solvent. Thus the active MgH_2 could be easily isolated in a pure form by filtration. We, therefore, decided to explore the general scope and utility of this reaction to produce magnesium hydride free from the alkali metal halide by-product. We also wished to determine if Li_nMgH_{2+n} is formed in the reaction and if so isolate the compound.

Experimental Section

All operations were carried out either in a nitrogen filled glove box equipped with a recirculating system to remove oxygen and water[6] or on the bench using typical Schlenk tube techniques. All glassware was flash flamed and flushed with nitrogen prior to use.

(6) T. L. Brown, D. W. Dickerhoof, D. A. Bafus and G. L. Morgan, Rev. Sci. Instrum., 33, 491 (1962).

Instrumentation. - Infrared spectra were obtained using a Perkin Elmer model 621 High Resolution Infrared Spectrophotometer. Cesium Iodide cells were used. Spectra of solids were obtained in nujol which had been dried over sodium wire and stored in a dry box.

X-ray powder diffraction patterns were run using a Debye-Scherrer camera of 114.6 mm diameter using CuK_{α} (1.540 Å) radiation with a nickel filter. Single walled capillaries of 0.5 mm diameter were used. These were filled in the dry box and sealed with a microburner.

Reagents. - Tetrahydrofuran and diethyl ether (Fisher Certified Reagent) were distilled over sodium aluminum hydride and lithium aluminum hydride, respectively, immediately before use.

Mercuric halides (Baker Analyzed) were dried under vacuum and used without further purification. Triply sublimed magnesium was obtained from Dow Chemical Co. It was washed with diethyl ether and dried under vacuum prior to use.

Sodium hydride was obtained from Alfa Inorganics as a 57% suspension in mineral oil. Lithium hydride was obtained from Alfa Inorganics as a dry powder. t-Butyl lithium in pentane solution was obtained from Foote Mineral Co.

Analytical Procedures. - Halogen analysis was carried out by the Volhard method. Magnesium analysis was carried out by titration with EDTA. Hydridic hydrogen analysis was carried out by hydrolyzing a weighed sample of the compound on a high vacuum line and transferring the gas to a calibrated measuring bulb with a Töpler pump after passing the gas through a liquid nitrogen trap. Lithium analysis was carried out by flame photometry.

Preparation of Magnesium Halides in Diethyl Ether and Tetrahydrofuran. - Magnesium halides in ether solvents were prepared as described previously.[7]

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(7) E. C. Ashby, R. D. Schwartz, and B. D. James, Inorg. Chem. 9, 325 (1970).

Preparation of Lithium Hydride. - To an autoclave (300 ml chamber) was added 150 ml of t-butyl lithium in pentane. The autoclave was then pressurized to 3000 psi with hydrogen and allowed to stir overnight at room temperature. The resulting solution was not filtered and the white solid obtained was never allowed to become dry. The supernatant liquid showed no activity and analysis of the solid as a slurry in pentane gave a lithium to hydrogen ratio of 1.0:1.0.

Reaction of Lithium Hydride (Commercial) with Magnesium Chloride in Tetrahydrofuran. - To 50 ml of magnesium chloride in THF (0.3188 m) was added 250 mg lithium hydride. The solution was allowed to stir for two days at room temperature. The solution was then filtered and the analysis of the filtrate gave a magnesium to chloride ratio of 1.0:1.97.

Reaction of Lithium Hydride (Commercial) with Magnesium Bromide in Tetrahydrofuran. - To 25 ml of magnesium bromide in tetrahydrofuran (0.1436 M) was added 50 mg of lithium hydride. The solution was allowed to stir for

two days at room temperature. The solution was then filtered and the analysis of the filtrate gave a magnesium to bromide ratio of 1.0:2.02.

In a separate experiment the lithium hydride was added to the magnesium bromide (in excess) and the resulting solution was refluxed for two days. The solution was then filtered and the analysis of the filtrate gave a magnesium to bromide ratio of 1.0:3.54. The infrared spectrum of the solid showed some broad bands in the region of 800 cm^{-1} - 600 cm^{-1} characteristic of magnesium hydride.

Reaction of Lithium Hydride (prepared from t-Butyl Li) and Magnesium Chloride in Tetrahydrofuran. - To 25 ml of magnesium chloride in THF (0.3258 m) was added 20 ml of a lithium hydride slurry (0.8 m) in THF. The solution was stirred for two days at room temperature. The solution was then filtered and the analysis of the filtrate gave a magnesium to chloride ratio of 1.0:2.02. Analysis of the solid obtained gave a H:Mg ratio of 1.0:0.1. The X-ray powder pattern of the solid showed only lines for lithium hydride.

Reaction of Lithium Hydride (prepared from t-butyl lithium) and Magnesium Bromide in Tetrahydrofuran. - To 75 ml magnesium bromide in THF (0.1841 m) was added 33 ml of a slurry of lithium hydride (0.8 m). The solution was stirred overnight. The solution was then filtered and the filtrate gave on analysis a magnesium to bromide ratio of 1.0:2.99. The X-ray powder pattern of the solid obtained showed strong lines corresponding to magnesium hydride and some very weak lines corresponding to lithium hydride. The infrared spectra of the solid also correspond to magnesium hydride.

Reaction of Sodium Hydride and Magnesium Bromide in Tetrahydrofuran. - To 83.4 ml of magnesium bromide in THF (0.1436 m) was added 1.15 g of sodium

hydride (57% in mineral oil) and stirred for two days. The solution was then filtered and the analysis of the filtrate showed no magnesium or bromide in solution. The infrared spectra and X-ray powder pattern indicate a mixture of sodium bromide and magnesium hydride.

Reaction of Sodium Hydride and Magnesium Chloride in Tetrahydrofuran. - To 50 ml of magnesium chloride in THF (0.3243 m) was added 1.5 g sodium hydride (57% in mineral oil). The solution was stirred for two days at room temperature and then filtered. The infrared spectrum and X-ray powder pattern of the solid indicated the solid to be a mixture of sodium chloride and magnesium hydride with some unreacted sodium hydride.

Reaction of Sodium Hydride and Magnesium Iodide in THF. - To 500 ml THF was added 120 ml of 0.1641 m magnesium iodide in diethyl ether. To this slurry of $MgI_2 \cdot 6THF$ was added 1.87 gm sodium hydride and the slurry stirred for three days. No iodine was detected in the supernatant solution after three days and the solution was filtered. An X-ray powder pattern of the resulting solid showed only sodium hydride and $MgI_2 \cdot 6THF$.

Reaction of Sodium Hydride and Magnesium Iodide in Diethyl Ether. - To 100 ml of magnesium iodide in diethyl ether (0.1629 m) was added 1.4565 gm of sodium hydride (57% in mineral oil). The solution was stirred for two days and then filtered. The infrared spectrum and X-ray powder pattern showed sodium iodide and magnesium hydride to be present. The solid was then placed in 200 ml of THF and stirred for one day. This solution was then filtered and the resulting solid analyzed for magnesium and iodine. The Mg:I ratio was 1.0:0.11. This represents removal of over 90% of the sodium iodide.

Results and Discussion

In the present study lithium hydride and sodium hydride were allowed to react with magnesium chloride and magnesium bromide in THF and with magnesium iodide in THF and diethyl ether. The purpose of this study was to prepare magnesium hydride quantitatively and free from alkalimetal halides where possible. This is desirable since the lithium hydride and magnesium halide starting materials are less expensive than the lithium aluminum hydride and diethyl magnesium frequently used.

Commercial lithium hydride obtained as a dry powder did not react with magnesium halides in THF at room temperature. Even after stirring at room temperature for several days only the unreacted starting materials were recovered. The nonreactivity of the commercial grade of lithium hydride is probably due to the formation of an oxide coat on the solid. In a preliminary experiment the commercial grade of lithium hydride was allowed to react with magnesium bromide in refluxing THF. Some reaction did take place as the Mg:Br ratio in solution rose to 1.0:3.54. The extent of this reaction is currently under study. Care however must be taken to guard against cleavage of the THF by the MgH_2.[8]

(8) H. E. Podall and W. E. Becker, J. Org. Chem., 23, 1848 (1958).

In order to avoid the problem of ether cleavage a more reactive form of lithium hydride was prepared which might reduce the time required for complete reaction and thus also reduce the cleavage. Hydrogenation of t-butyl lithium in pentane at 3000 psi and 25°C afforded a reactive LiH as a pentane slurry. The LiH remained active as long as it was not allowed to become dry.

Reaction of this LiH with $MgCl_2$ in THF at 25°C however afforded only unreacted starting material after two days. The reaction of this LiH with $MgBr_2$ in THF gave MgH_2 after stirring over night. The reaction was not complete however since some weak lines corresponding to LiH were found along with lines for MgH_2 in the X-ray powder pattern of the solid product.

The main advantage of using LiH is that the lithium halide by-products would be soluble in both diethyl ether and THF. But if one must obtain the LiH from t-butyl lithium then the economics of the reaction would no longer be an advantage. With this in mind we decided to use the commercially available sodium hydride which is a 50% dispersion in mineral oil. Since it is sold as a dispersion, the sodium hydride is able to retain its reactivity. Sodium hydride readily reacts with $MgBr_2$ in THF to yield MgH_2. If excess $MgBr_2$ is used no sodium hydride is found in the solid product. However the MgH_2 produced is mixed with two moles of the insoluble NaX by-product. However for many purposes this will cause no difficulty.

Sodium hydride was found not to react with MgI_2 in THF. It was thought that the solubility of the NaI in THF would provide a driving force for the reaction but after stirring for several days only starting materials were recovered. Sodium hydride was found to react with MgI_2 in diethyl ether. Ninety percent of the diethyl ether insoluble NaI was removed simply by stirring the physical mixture of MgH_2 and NaI in THF.

In conclusion it may be noted that where excess alkali metal hydride was used no complex of the form M_nMgH_{2+n} was detected but only physical mixtures of the alkalimetal hydride and magnesium hydride as shown by the X-ray powder diffraction patterns.

Table I. Summary of Results of Reactions of Metal Hydrides with Magnesium Halides in Ether Solvents.

Reactants	Solvent	Reaction Conditions	Yield MgH_2
NaH/MgI_2	$(C_2H_5)_2O$	Room Temp.; 2 days	100% (a)
NaH/MgI_2	THF	Room Temp.; 3 days	No reaction
$NaH/MgBr_2$	THF	Room Temp.; 2 days	100%
$NaH/MgCl_2$	THF	Room Temp.; 2 days	50%
$LiH/MgCl_2$	THF	Room Temp.; 2 days	No reaction
$LiH/MgBr_2$	THF	Reflux; 2 days	33%
$LiH/MgCl_2$ (b)	THF	Room Temp.; 2 days	No reaction
$LiH/MgBr_2$ (b)	THF	Room Temp.; 1 day	33%
KH/MgI_2	$(C_2H_5)_2O$	Reflux; 1 day	100%

(a) NaI can be removed by extraction with THF.

(b) LiH prepared by hydrogenation of t-butyl lithium.

Concerning the Reactions of Lithium and Sodium Aluminum Hydride with Grignard Reagents in Ether Solution. Attempts to Prepare $RMgAlH_4$ Precursors to $HMgAlH_4$.

E. C. Ashby and R. D. Schwartz

Abstract

The reaction of lithium aluminum hydride and n-butylmagnesium chloride in diethyl ether yields a compound which on the basis of its infrared spectra is assigned the formula $HMgAlH_3R$. This compound is soluble in ether solvents but insoluble in hydrocarbon solvents such as octane. Reaction of lithium or sodium aluminum hydride with methyl or sec-butyl magnesium chloride does not result in the formation of $HMgAlH_3R$ but instead magnesium hydride is produced.

Introduction

In our attempts to prepare hydridomagnesium aluminum hydride ($HMgAlH_4$) we have focused attention on the preparation of alkyl magnesium aluminum hydrides since this class of compounds should be easily converted to $HMgAlH_4$ by hydrogenation. The method we chose to prepare this precursor involves the reaction of lithium aluminum hydride and a Grignard reagent.

$$LiAlH_4 + RMgX \rightarrow RMgAlH_4 + LiX \qquad (1)$$

$$RMgAlH_4 \xrightarrow{H_2} HMgAlH_4 + H_2 \qquad (2)$$

Strebel[1] has reported that addition of lithium aluminum hydride to

(1) P. Strebel, Ph.D. Dissertation, University of Munich, 1958.

ethyl magnesium chloride in diethyl ether yielded a soluble compound with the empirical formula $C_2H_5MgAlH_4$ and the structure he assigned to it is shown in Figure I. However no spectral data were reported to verify this structure.

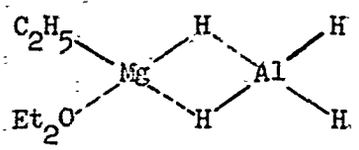

Figure I

In 1956 Rice[2] reported that when phenylmagnesium bromide was allowed to

(2) H. J. Rice and P. J. Andrelles, Technical Report to the Office of Naval Research Contract ONR-494(04), 1956.

react with lithium aluminum hydride in diethyl ether at a mole ratio of 6:1, the resulting product had the empirical formula $(C_6H_5)_2Mg \cdot C_6H_5MgH \cdot 3(C_2H_5)_2O$. When a Grignard to lithium aluminum hydride ratio of 10:1 was used, a product of empirical formula $C_6H_5MgBr \cdot C_6H_5MgH \cdot 3(C_2H_5)_2O$ was isolated. These compounds were soluble in benzene and insoluble in diethyl ether.

Considering these differences in the prior art and our desire to prepare $RMgAlH_4$ compounds we decided to study the reactions of alkali metal aluminum hydrides with Grignard reagents in order to determine the exact course of this reaction.

Experimental Section

All operations were carried out either in a nitrogen filled glove box

equipped with a recirculating system to remove oxygen and water[3] or on the

(3) T. L. Brown, D. W. Dickerhoof, D. A. Bafus and G. L. Morgan, Rev. Sci. Instrum., 33, 491 (1962).

bench using typical Schlenk tube techniques. All glassware was flash flamed and flushed with nitrogen prior to use.

Instrumentation. - Infrared spectra were obtained using a Perkin Elmer model 621 High Resolution Infrared Spectrophotometer. Cesium Iodide cells were used. X-ray powder diffraction patterns were run using a Debye-Scherrer camera of 114.6 mm diameter using CuK_{α} (1.540 A) radiation with a nickel filter. Single walled capillaries of 0.5 mm diameter were used. These were filled in the dry box and sealed with a microburner.

Reagents. - Diethyl ether (Fisher Certified reagent) was distilled over lithium aluminum hydride immediately prior to use. Triply sublimed magnesium was obtained from Dow Chemical Co. The magnesium was washed with diethyl ether and dried under vacuum prior to use. Lithium and sodium aluminum hydride were obtained from Ventron Metal Hydrides Division. Lithium aluminum hydride solutions in diethyl ether were prepared as described previously.[4] Sodium aluminum hydride

(4) E. C. Ashby, R. D. Schwartz, and B. D. James, Inorg. Chem. 9, 325, (1970).

was recrystallized from diethyl ether - THF mixtures.

Analytical Procedures. - Halogen analysis was carried out by the Volhard method. Aluminum analysis was carried out by titration with EDTA. Magnesium analysis in the presence of aluminum was carried out by masking the aluminum with

triethanolamine and titrating the magnesium with EDTA. Hydridic hydrogen was measured by hydrolyzing a weighed sample on a high vacuum line and transferring the gas to a calibrated bulb via a Töpler pump after passing the gas through a liquid nitrogen trap.

Reaction of Lithium Aluminum Hydride and n-Butyl Magnesium Chloride in Diethyl Ether. - To 45.06 mmoles of lithium aluminum hydride was added 150 ml diethyl ether. To this solution was added 28.71 ml of n-butyl magnesium chloride in diethyl ether (1.5642 m). The solution was stirred over night at room temperature. The solution was filtered and 1.6661 gm of solid isolated which gave on analysis: Cl:74.83, Mg:2.98, Al:0.99. The clear filtrate gave the following analysis: Mg:Al:Cl, 1.0:1.02:0.1. The solution contained 95% of the initial amount of magnesium. The infrared spectrum of the filtrate showed bands at 1765 cm^{-1} (broad); 720 cm^{-1}; 680 cm^{-1} (sh). In a separate experiment the solvent was removed from the filtrate and the resulting solid gave an infrared spectrum with bands at 1760 cm^{-1} (broad) and 720 cm^{-1}. The X-ray powder pattern of the solid showed no lines for magnesium hydride. When this solid was dissolved in THF its infrared spectrum gave bands at 1700 cm^{-1}; 790 cm^{-1}; 755 cm^{-1}.

Reaction of sec-Butyl Magnesium Chloride and Lithium Aluminum Hydride in Diethyl Ether. - To 10 ml s-butyl magnesium chloride in diethyl ether (2.41 m) was added 14.19 ml of lithium aluminum hydride in diethyl ether (1.6981 m). The solution was stirred over night. The solution was filtered and 1.1552 gm of solid was isolated. The solid on analysis gave a Mg:Al:Cl ratio of 1.0:0.02:0.85. The amount of magnesium with solid represented 65% of the initial magnesium. The infrared spectrum of this solid showed it to contain magnesium hydride. Analysis of the solution gave a Mg:Al ratio of approximately 2.0:3.0.

Reaction of sec-Butyl Magnesium Chloride and Sodium Aluminum Hydride in Diethyl Ether. - To 10 ml s-butyl magnesium chloride (2.41 m) was added 100 ml diethyl ether and 1.3605 gm sodium aluminum hydride. The solution was stirred for two days. The solution was then filtered and the clear filtrate gave on analysis a Mg:Al ratio of 1.0:1.67. The infrared spectrum of the filtrate showed broad bands centered at 1780 cm^{-1} and 720 cm^{-1}. The resulting solid gave on analysis a Mg:Al:Cl ratio of 1.0:0.3:2.0. This represents 50.8% of the initial amount of magnesium. The infrared spectrum of the solid showed it to contain magnesium hydride.

Reaction of Sodium Aluminum Hydride and Methyl Magnesium Bromide. - To 11.79 mmoles of sodium aluminum hydride was added 20.68 ml of methyl magnesium bromide in diethyl ether (0.5701 m). The solution was stirred for two days and filtered. The resulting clear filtrate gave on analysis a Mg:Al ratio of 1.0:2.12. The infrared spectrum of the filtrate gave weak bands at 710 cm^{-1} and 615 cm^{-1}. The resulting solid gave on analysis a Br:Mg:Al ratio of 2.0:0.9:1.0. This represents 82.8% of the initial amount of magnesium. The infrared spectrum of the solid gave bands at 1680 cm^{-1} (broad) and 710 cm^{-1} (broad) and also bands corresponding to magnesium hydride.

Results and Discussion

In this paper we would like to report the preliminary results which we have obtained in our study of the reactions of Grignard reagents with alkali metal aluminum hydrides.

n-Butylmagnesium chloride was allowed to react with lithium aluminum hydride in diethyl ether at a mole ratio of 1:1. A solid was obtained by

filtering the reaction mixture which was shown by elemental analysis and X-ray powder patterns to be lithium chloride. Analysis of the filtrate gave a Mg:Al ratio of 1.0:1.02 and the amount of magnesium in solution represented 95% of the original magnesium. The infrared spectrum of the filtrate showed broad bands at 1765 cm^{-1}; 780 cm^{-1} and a shoulder at 680 cm^{-1}. No bands were observed in the Mg-C stretching region of 500-535 cm^{-1}. We have concluded therefore that the alkyl group is bonded to aluminum and not magnesium. The compound $HMgAlH_3R$ was found to be soluble in diethyl ether and THF but insoluble in hydrocarbon solvents such as octane.

Attempts to hydrogenate $HMgAlH_3R$ to $HMgAlH_4$ have not been successful.

$$HMgAlH_3R \xrightarrow{H_2} HMgAlH_4$$

In the reaction of lithium aluminum hydride with sec-butyl magnesium chloride in 1.0:1.0 molar ratio, a solid was obtained which was shown to contain magnesium hydride. The Mg Al ratio in solution was found to be 2:3. In the reaction of sodium aluminum hydride with sec-butyl magnesium chloride similar results were obtained. The infrared spectrum of the solution gave broad bands at 1780 cm^{-1} and 720 cm^{-1}. The infrared spectrum of the solid product showed it to contain magnesium hydride. We had hoped to prepare methyl magnesium aluminum hydride by the reaction of sodium aluminum hydride with methyl magnesium bromide in diethyl ether in order to look at the NMR. However a solid was obtained from this reaction which had a Mg Al ratio of 0.9:1.0. The infrared spectrum of the solid gave broad bands at 1680 cm^{-1} and 710 cm^{-1} and also bands corresponding to magnesium hydride.

The reactions of alkali metal aluminum hydrides with Grignard reagents do not seem to be straight forward. In some cases a compound of the empirical formula $HMgAlH_3R$ was produced and in other cases magnesium hydride is the major product. In our future studies of this system we intend to look at the effects of solvent and of the solubility of the alkalimetal halide by-products as well as the effects of varying the alkyl group on the nature of the reaction product produced. The two different reaction paths are proposed below.

Path I

$$LiAlH_4 + n\text{-}BuMgCl \rightarrow LiCl\downarrow + n\text{-}BuMgAlH_4 \rightleftarrows HMgAlH_3(n\text{-}Bu)$$

Path II

(A) $$LiAlH_4 + s\text{-}BuMgCl \rightarrow LiCl\downarrow + s\text{-}BuMgAlH_4 \rightleftarrows HMgAlH_3(s\text{-}Bu) \rightleftarrows 1/2\ MgH_2\downarrow + Mg[AlH_3(s\text{-}Bu)]_2$$

(B)

$$LiAlH_4 + \begin{cases} s\text{-}BuMgCl \rightarrow LiCl\downarrow + sBuMgAlH_4 \rightarrow HMgAlH_3(s\text{-}Bu) \\ \rightleftarrows \\ s\text{-}Bu_2Mg \rightarrow MgH_2 + LiAl(s\text{-}Bu)_2H_2 \\ + \\ MgCl_2 \rightarrow LiCl\downarrow + ClMgAlH_4 + Mg(AlH_4)_2 \end{cases}$$

It would appear that running the reaction in Et_2O rather than THF where the Schlenk equilibrium lies further to RMgX side would have the best chance

of forming $RMgAlH_4$. Such a compound would also have a better chance of stability rather than disproportionation if the transformation is carried out in benzene using $RMgX \cdot NR_3$.[5]

(5) E. C. Ashby and R. Reed, J. Org. Chem., 31, 985 (1966).

$$s\text{-BuCl} + Mg \xrightarrow[PhH]{Et_3N} s\text{-BuMgCl} \cdot NEt_3$$

$$NR_4AlH_4 + s\text{-BuMgCl} \cdot NEt_3 \xrightarrow{PhH} NR_4Cl\downarrow + s\text{-BuMgAlH}_4 \cdot NEt_3$$

$$\downarrow H_2$$

$$HMgAlH_4 + C_4H_{10}$$

Concerning the Preparation of $HMgAlH_4$ and $HMgBH_4$

E. C. Ashby and R. D. Schwartz

Abstract

Efforts to date to prepare hydridomagnesium aluminum hydride and hydrido magnesium borohydride have resulted in physical mixtures of magnesium hydride and magnesium aluminum hydride or magnesium borohydride. The attempts made so far have included pyrolysis and hydrogenolysis of alkyl magnesium aluminum hydride and alkyl magnesium borohydride and the reduction with sodium hydride of chloromagnesium aluminum hydride and chloromagnesium borohydride.

Introduction

The preparation of compounds of the type $HMBH_4$ and $HMAlH_4$ have been investigated previously. In 1940 Burg and Schlesinger[1] reported the preparation of $HBeBH_4 \cdot N(CH_3)_3$ by borane extraction from $Be(BH_4)_2$ by trimethylamine.

$$Be(BH_4)_2 + 2[N(CH_3)_3] \rightarrow HBeBH_4 \cdot N(CH_3)_3 + BH_3N(CH_3)_3 \qquad (1)$$

In 1951 Schlesinger[2] and coworkers reported that the addition of diethyl magnesium to a large excess of lithium aluminum hydride in diethyl ether followed

(1) A. B. Burg and H. I. Schlesinger, J. Am. Chem. Soc., 62, 3425 (1940).

(2) G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilzbach, and H. I. Schlesinger, J. Am. Chem. Soc., 73, 4585 (1951).

by addition of benzene resulted in the precipitation of a solid with the empirical formula $HMgAlH_4$. The compound was not characterized further.

$$LiAlH_4 + Mg(C_2H_5)_2 \rightarrow HMgAlH_4 + \text{other products}$$

In this paper we would like to report on our attempts to date to prepare and characterize $HMgAlH_4$ and $HMgBH_4$.

Experimental Section

All operations were carried out either in a nitrogen filled glove box equipped with a recirculating system to remove oxygen and water[3] or at the

(3) T. L. Brown, D. W. Dickerhoof, D. A. Bafus and G. L. Morgan, Rev. Sci. Instrum., 33, 491 (1962).

bench using typical Schlenk tube techniques. All glassware was flash flamed and flushed with nitrogen prior to use.

Instrumentation. - Infrared spectra were obtained using a Perkin Elmer model 621 High Resolution Infrared Spectrophotometer. Cesium iodide cells were used.

X-ray powder diffraction patterns were run using a Debye-Scherrer camera of 114.6 mm diameter using CuK_α (1.540 A) radiation with a nickel filter. Single walled capillaries of 0.5 mm diameter were used. These were filled in the dry box and sealed with a microburner.

Reagents. - Tetrahydrofuran and benzene (Fisher Certified reagent) were distilled over sodium aluminum hydride immediately prior to use. Diethyl ether (Fisher Certified reagent) was distilled over lithium aluminum hydride

immediately prior to use.

Mercuric halides (Baker Analyzed) were dried under vacuum and used without further purification. Triply sublimed magnesium was obtained from Dow Chemical Co. It was washed with diethyl ether and dried under vacuum prior to use.

Lithium and sodium aluminum hydride, sodium hydride (57% suspension in mineral oil) and sodium borohydride were obtained from Ventron Metal Hydrides Division.

Magnesium aluminum hydride, chloromagnesium aluminum hydride, iodomagnesium aluminum hydride and magnesium halide were prepared as described previously.[4]

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(4) E. C. Ashby, R. D. Schwartz and B. D. James, Inorg. Chem., 9, 325 (1970).

Analytical Procedures. - Halogen analysis was carried out by the Volhard method. Aluminum and magnesium analyses were carried out by titration with EDTA. Magnesium analysis in the presence of aluminum was carried out by masking the aluminum with triethanol amine. Lithium analysis was carried out by flame photometry. Hydridic hydrogen was analyzed by hydrolyzing a weighed sample of the compound on a high vacuum line and transferring the gas to a calibrated bulb via a Töpler pump after passing the gas through a liquid nitrogen trap.

Preparation of Lithium Hydride. - To an autoclave (300 ml chamber) was added 150 ml of t-butyl lithium in pentane. The autoclave was then pressurized to 3000 psi and allowed to stir over night at room temperature. The resulting solution was not filtered and the white solid obtained was not allowed to become dry. The supernatant liquid showed no activity and the analysis of the solid as a slurry in pentane gave a lithium to hydrogen ratio of 1.0 1.0.

Preparation of Ethyl and sec-Butyl Magnesium Borohydride. - Ethyl magnesium borohydride was prepared as described previously.[5] In the preparation

(5) W. E. Becker and E. C. Ashby, Inorg. Chem., 4, 1816 (1965).

of sec-butyl magnesium borohydride 2.41 gm of sodium borohydride was added to 50 ml of sec-butyl magnesium chloride in Et_2O (1.09 m). This was diluted with 50 ml of diethyl ether. The solution was stirred for two days. The solution was filtered and the analysis of the filtrate gave a Mg:Cl ratio of 1.0:0.02. The infrared spectrum of the solution gave bands at 2420 cm^{-1}, 2220 cm^{-1} and 535 cm^{-1}.

Preparation of n-Butyl Magnesium Aluminum Hydride. - To 45.06 mmole of lithium aluminum hydride was added 150 ml of diethyl ether. To this was added 28.71 ml of n-butyl magnesium chloride in diethyl ether (1.5642 m). The solution was stirred over night at room temperature. The solution was filtered and the filtrate gave the following analysis: Mg:Al:Cl; 1.0:1.02:0.1. The infrared spectrum of the filtrate gave bands at 1765 cm^{-1} (broad); 780 cm^{-1}; 680 cm^{-1} (sh).

Reaction of Sodium Hydride and Chloromagnesium Hydride in Tetrahydrofuran. - To 50 ml of chloromagnesium aluminum hydride in THF (0.2056 m) was added 454.5 mg sodium hydride (57% dispersion in mineral oil). The solution was stirred for two days. The solution was then filtered and the filtrate gave on analysis a Cl/Mg/Al ratio of 0.0:1.0:1.88. From the filtration was isolated 1.9601 gm of solid. The infrared spectrum of the solid gave bands at 1725 cm^{-1}; 1025 cm^{-1}; 975 cm^{-1}; 790 cm^{-1}; 745 cm^{-1}. The X-ray powder pattern of the solid gave lines corresponding to sodium chloride, magnesium aluminum hydride and magnesium hydride.

Reaction of Sodium Hydride and Magnesium Aluminum Hydride in Tetrahydrofuran. - To 75 ml of THF was added 4.3028 gm of $Mg(AlH_4)_2 \cdot 4THF$ and 677.7 mg of sodium hydride (57% dispersion in mineral oil). The solution was stirred for two days The solution was filtered and the filtrate contained aluminum but no magnesium The amount of aluminum in solution corresponded to the amount of sodium hydride added The infrared spectrum of the filtrate showed bands at 1680 cm^{-1} and 772 cm^{-1} The solid resulting from the filtration gave an infrared spectrum with bands at 1725 cm^{-1}, 1025 cm^{-1}, 795 cm^{-1}; 745 cm^{-1}

Reaction of Lithium Hydride and Iodomagnesium Aluminum Hydride in Diethyl Ether - To iodomagnesium aluminum hydride was added excess lithium hydride as a slurry in pentane. The solution was stirred for several days. The solution was filtered and the analysis of the filtrate gave an I:Mg:Al ratio of 1 52.0.0 1 CO. The infrared spectrum of the solution showed bands at 1740 cm^{-1} and 760 cm^{-1}. The solid obtained from the filtration gave an infrared spectrum and an X-ray powder pattern corresponding to magnesium hydride

Reaction of Sodium Hydride and Chloromagnesium Borohydride in Tetrahydrofuran - To 45 ml of chloromagnesium borohydride in THF (0.4887 m) was added 1.9254 gm of sodium hydride (57% dispersion in mineral oil). The solution was stirred for two days. It was then filtered. The infrared spectrum of the filtrate showed no bands other than THF. The X-ray powder pattern of the solid resulting from the filtration gave lines corresponding to sodium chloride, sodium borohydride and magnesium hydride. The infrared spectrum of the solid gave bands corresponding to sodium borohydride and magnesium hydride

Pyrolysis of n-Butyl Magnesium Aluminum Hydride. - To 100 ml of light mineral oil (dried over sodium wire) was added 25 ml of n-butyl magnesium aluminum

hydride in diethyl ether (0.34 m). The ether was stripped off and the n-butyl magnesium aluminum hydride was insoluble in the mineral oil. The mineral oil was then heated to 80° under vacuum for several hours. At the end of this time the reaction was cooled and filtered and washed with benzene. The solid obtained gave an infrared spectrum with bands at 1860 cm^{-1} (sh); 1745 cm^{-1}; 1700 cm^{-1} (sh); 920 cm^{-1} and 715 cm^{-1}. The analysis of the product gave a H/Butane/Mg ratio of 4.17 1.0:1.0.

Pyrolysis of Ethyl Magnesium Borohydride. - The solvent was removed from 25 ml of ethyl magnesium borohydride in THF (2.5 m) and to the resulting oil was added 100 ml of heavy mineral oil. The ethyl magnesium borohydride was missible in the mineral oil. The solution was then heated slowly to a temperature of 170°C with an oil bath. At this temperature a gas was given off and a solid was formed. After two hours the solution was allowed to cool to room temperature. The solution was filtered and the solid obtained was washed with benzene. The analysis of the solid gave a Mg:H ratio of 1.0:3.74 and no ethane. The infrared spectrum of the solid showed bands for magnesium hydride and some bands at 2270 cm^{-1} with a shoulder at 2380 cm^{-1}. The X-ray powder pattern showed strong lines corresponding to magnesium hydride and some other weak lines.

Pyrolysis of sec-Butyl Magnesium Borohydride. - The diethyl ether was removed from 25 ml of a s-butyl magnesium borohydride solution (0.3040 m) and to the resulting oil was added 100 ml octane. The solution was heated to 80°C under vacuum. The solution was cooled and filtered and the solid obtained gave lines for magnesium hydride and some other lines. In a separate experiment s-butyl magnesium borohydride was heated to 105°C under vacuum in heavy mineral oil. A yellow oil was obtained which was not characterized further.

Hydrogenolysis of n-Butyl Magnesium Aluminum Hydride in Diethyl Ether. - To 35 ml of n-butyl magnesium aluminum hydride was added 65 ml diethyl ether. This solution was placed in the autoclave (300 ml chamber). The sample was pressurized to 3000 psi and stirred at 25°C over night. However no reaction took place. The autoclave was repressurized to 3000 psi and stirred at 50°C over night. A white solid was obtained from this reaction. The solution was filtered and the filtrate gave on analysis a Mg:Al ratio of 1.0:2.33. The infrared spectrum of the filtrate gave bands at 670 cm^{-1} and a shoulder at 700 cm^{-1}. The gray solid obtained from the filtration gave on analysis a Mg:Al:H ratio of 1.0:0.3·2.63. The infrared spectrum of the solid corresponded to magnesium hydride. The X-ray powder pattern gave lines corresponding to magnesium hydride and also some other lines.

Hydrogenolysis of sec-Butyl Magnesium Borohydride. - To 75 ml diethyl ether in the autoclave was added 25 ml of s-butyl magnesium borohydride in ether (0 6184 m). The autoclave was pressurized to 2000 psi and the solution stirred over night at 25°C. No reaction was observed. The autoclave was repressurized to 3000 psi and the solution stirred at 50°C over night. The solution was filtered and the infrared spectrum of the filtrate gave bands at 2450 cm^{-1}; 2220 cm^{-1}; and 540 cm^{-1} (sh). The infrared spectrum of the white solid corresponded to magnesium hydride. No bands were observed between 2000-2500 cm^{-1}. The X-ray powder pattern of the solid gives lines for magnesium hydride only. The weight of the solid corresponds to a nearly quantitative yield of magnesium hydride.

A similar experiment was run with benzene as the solvent. The results were the same. That is a solid was obtained with a X-ray powder pattern and

infrared spectrum corresponding to magnesium hydride and bands in the infrared spectrum of the filtrate at 2450 cm^{-1} and 2220 cm^{-1}.

Results and Discussion

The reactions employed in the attempt to prepare $HMgAlH_4$ or $HMgBH_4$ can be divided into three general categories. The first is the reduction of a compound of empirical formula $ClMgAlH_4$ or $ClMgBH_4$ by a chemical source of hydride ion (eg. NaH). The second method is the pyrolysis in some diluent of a compound with the empirical formula $RMgAlH_4$ or $RMgBH_4$. The third method is the high pressure hydrogenation of $RMgAlH_4$ or $RMgBH_4$ in the autoclave.

With reference to the first case, sodium hydride was allowed to react with chloromagnesium aluminum hydride in THF at a molar ratio of 1:1. After two days the solution was filtered. The elemental analysis of the filtrate gave a Cl:Mg:Al ratio of 0.0:1.0:1.88. The solid isolated by this filtration had an infrared spectrum with bands at 1725 cm^{-1}, 1025 cm^{-1}, 975 cm^{-1}, 790 cm^{-1} and 745 cm^{-1} corresponding to $Mg(AlH_4)_2 \cdot 4THF$. The X-ray powder pattern of the solid confirmed that it was a physical mixture of sodium chloride, magnesium hydride and magnesium aluminum hydride. When sodium hydride was added in excess to chloromagnesium aluminum hydride, the infrared spectrum of the filtrate showed sodium aluminum hydride to be present in the solution. The solid resulting from this was a mixture of sodium chloride and magnesium hydride. It was felt that the formation of sodium aluminum hydride was the result of alane abstraction from magnesium aluminum hydride by sodium hydride. To test this sodium hydride was allowed to react with magnesium aluminum hydride in THF in a molar ratio of 1:1. The quantitative formation of sodium aluminum hydride (based on sodium hydride)

resulted. The solid product was a physical mixture of magnesium hydride and magnesium aluminum hydride. The conclusion here is that $HMgAlH_4$ disproportionates in THF.

$$NaH + ClMgAlH_4 \rightarrow NaCl\downarrow + HMgAlH_4 \xrightarrow{NaH} MgH_2\downarrow + NaAlH_4 \quad (3)$$

$$NaH + Mg(AlH_4)_2 \xrightarrow{THF} NaAlH_4 + HMgAlH_4 \rightarrow 1/2\ MgH_2\downarrow + Mg(AlH_4)_2\downarrow \quad (4)$$

Lithium hydride was added in excess as a pentane slurry to iodomagnesium aluminum hydride in diethyl ether. The solution was filtered after several days and the elemental analysis of the filtrate gave an I:Mg:Al ratio of 1.52:0.0:1.0. The infrared spectrum of the filtrate gave bands at 1740 and 760 cm^{-1} corresponding to lithium aluminum hydride. The infrared spectrum and X-ray powder pattern of the solid corresponded to magnesium hydride. We intend to run this reaction in a one:one molar ratio to prepare $HMgAlH_4$ in the hopes that it will be stable toward disproportionation in diethyl ether.

$$LiH + IMgAlH_4 \xrightarrow{Et_2O} \underset{\text{(soluble)}}{LiI} + \underset{\text{(insoluble)}}{HMgAlH_4\downarrow} (?) \quad (5)$$

Sodium hydride in excess was allowed to react with chloromagnesium borohydride in THF. The resulting solid was shown by X-ray powder patterns to be a mixture of sodium chloride, sodium borohydride and magnesium hydride.

$$NaH\ (excess) + ClMgBH_4 \xrightarrow{THF} NaCl + NaBH_4 + MgH_2 \qquad (6)$$

In the pyrolysis experiments n-butylmagnesium aluminum hydride as the diethyl etherate was suspended in light mineral oil. This slurry was heated under vacuum to 80°C for several hours however only unreacted starting material was recovered. Similar results were obtained in octane solution.

Ethylmagnesium borohydride was obtained as the THF solvate and was dissolved in 100 ml of heavy mineral oil. This solution was heated slowly to a temperature of 170°. At this point a gas was evolved and a solid formed. The solid obtained was filtered and washed with benzene. Elemental analysis gave a Mg:H ratio of 1.0:3.54 with no ethane. The infrared spectrum of the solid gave bands at 2270 and 2380 cm^{-1}. The X-ray powder pattern showed strong lines for magnesium hydride and some other weak lines.

The pyrolysis of sec-butylmagnesium borohydride was attempted since the sec-butyl group could be removed at a lower temperature. Sec-butylmagnesium borohydride as the diethyl ether solvate was dissolved in octane and heated to 80°C under vacuum. A solid was obtained which lines in the X-ray powder pattern corresponded to magnesium hydride plus some other lines.

The hydrogenolysis of n-butylmagnesium aluminum hydride in diethyl ether was carried out at 3000 psi hydrogen and 50°C. The solution was filtered and the elemental analysis of the filtrate gave a Mg:Al ratio of 1.0:2.33. The infrared spectrum of the filtrate gave bands in the Al-C stretching region at 670 cm^{-1} and a shoulder at 700 cm^{-1}. No bands were observed in the Al-H stretching region. The solid obtained from this filtration gave on analysis a Mg:Al:H ratio of 1.0:0.3:.63. The infrared spectrum of the solid corresponded

to magnesium hydride and no bands in the Al-H stretching region were observed. The X-ray powder pattern corresponded to magnesium hydride. It is not clear what is happening in this reaction. From hydrogenation of a $RMgAlH_4$ compound one would have expected to find at least a mixture of MgH_2 and $Mg(AlH_4)_2$. However while the MgH_2 was detected no $Mg(AlH_4)_2$ was found. The other products found may have been ether cleavage products although the conditions seem too mild for this.

The results of the hydrogenolysis of sec-butylmagnesium borohydride in both diethyl ether and benzene are straight forward. The solid obtained from this reaction in diethyl ether had an infrared spectrum corresponding to magnesium hydride, no bands in the boron-hydrogen stretching region were observed. The X-ray powder pattern gave strong lines corresponding to magnesium hydride and no other lines. The weight of the solid obtained corresponds to a quantitative yield of magnesium hydride. The filtrate from this reaction gave infrared bands at 2450 cm^{-1} and 2220 cm^{-1} corresponding to a $Mg(BH_4)_2$ species.

$$2(s\text{-}BuMgBH_4) \xrightarrow{H_2} MgH_2\downarrow + Mg(BH_4)_2 + C_4H_{10} \qquad (7)$$

When the reaction was run in benzene similar results were obtained. That is, a solid consisting of magnesium hydride and magnesium borohydride in solution.

Although the nature of the sec-butyl magnesium borohydride in solution is not known, it is clear that hydrogenolysis of this compound does not produce hydridomagnesium borohydride but a mixture of magnesium hydride and magnesium borohydride. This result also establishes the point that magnesium hydride

and magnesium borohydride will not redistribute in solution to yield hydridomagnesium borohydride.

Further work is in progress.

Concerning the Preparation of $Mg(AlH_4)(BH_4)$ and $MMg(AlH_4)_3$

E. C. Ashby and R. D. Schwartz

Abstract

The reactions of sodium aluminum hydride with chloromagnesium borohydride and of sodium borohydride with chloromagnesium aluminum hydride in THF produced mixtures of magnesium aluminum hydride and magnesium borohydride. Magnesium aluminum hydride and magnesium borohydride were found not to redistribute in THF or benzene. Trioctylpropylammonium aluminum hydride reacted with magnesium aluminum hydride in refluxing benzene to yield a solid which proved to be magnesium hydride.

Introduction

Unsymmetrical magnesium compounds are of course well known.[1] Some of our work[2] has afforded us compounds which would be the obvious precursors to $Mg(AlH_4)BH_4$. We therefore determined to examine the possibilities of preparing this compound.

Recently Rice and Ehrlich[3] reported the preparation of lithium beryllium

(1) G. E. Coates, M. L. H. Green, K. Wade, "Organometallic Compounds," Vol. I, Methuen and Co. Ltd. London, 1967, p. 76.

(2) E. C. Ashby, R. D. Schwartz and B. D. James, Inorg. Chem., 9, 325 (1970).

(3) G. Rice and R. Ehrlich, U. S. Patent 3,383,187 (1968).

aluminum hydride [$LiBe(AlH_4)_3$]. We have examined the possibility of preparing the compound $MMg(AlH_4)_3$ where M is lithium, sodium or tetraalkylammonium.

Experimental Section

All operations were carried out either in a nitrogen filled glove box equipped with a recirculating system to remove oxygen and water[4] or on the bench using typical Schlenk tube techniques. All glassware was flash flamed and flushed with nitrogen prior to use.

(4) T. L. Brown, D. W. Dickerhoof, D. A. Bafus and G. L. Morgan, Rev. Sci. Instrum., 33, 491 (1962).

Instrumentation. - Infrared spectra were obtained using a Perkin Elmer model 621 High Resolution Infrared Spectrophotometer. Cesium Iodide cells were used. Spectra of solids were obtained in nujol which had been dried over sodium wire and stored in a dry box.

X-ray powder diffraction patterns were run using a Debye-Scherrer camera of 114.6 mm diameter using CuK_α (1.5 OA) radiation with a nickel filter. Single walled capillaries of 0.5 mm diameter were used. These were filled in the dry box and sealed with a microburner.

Reagents. - Tetrahydrofuran and benzene (Fisher Certified reagent) were distilled over sodium aluminum hydride immediately before use.

Mercuric halides (Baker Analyzed) were dried under vacuum and used without further purification. Triply sublimed magnesium was obtained from Dow Chemical Co. It was washed with diethyl ether and dried under vacuum prior to use.

Sodium aluminum hydride and sodium borohydride were obtained from Ventron Metal Hydrides Division. The magnesium halides, magnesium aluminum

hydride and chloromagnesium aluminum hydride were prepared as described previously.[2]

Tri-n-octyl-n-propyl ammonium aluminum hydride was also prepared as described previously.[5]

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(5) R. Ehrlich, A. R. Young, and D. D. Perry, Inorg. Chem., 4, 758 (1965).

Analytical Procedures. - Halogen analysis was carried out by the Volhard method. Aluminum analysis was carried out by titration with EDTA. Magnesium analysis in the presence of aluminum was carried out by masking the aluminum with triethanol amine and titrating the magnesium with EDTA. Hydridic hydrogen was measured by hydrolyzing a weighed sample on a high vacuum line and transferring the gas to a calibrated bulb via a Töpler pump after passing the gas through a liquid nitrogen trap.

Preparation of Chloromagnesium Borohydride in Tetrahydrofuran. - To 118.5 ml of magnesium chloride in THF (0.4822 m) was added 2.5585 gm of sodium borohydride. The solution was stirred for two days. The solution was then filtered and the filtrate analyzed for magnesium and chloride. This analysis gave a Mg:Cl ratio in solution of 1.00:1.07. The infrared spectrum of the solution showed bonds at 2175 and 2380 cm^{-1}.[6]

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(6) W. E. Becker and E. C. Ashby, Inorg. Chem., 4, 1616 (1965).

Preparation of Magnesium Borohydride in Tetrahydrofuran. - To 55 ml of magnesium chloride in THF (0.3366 m) was added 1.4207 gm of sodium borohydride. The solution was stirred for two days and then filtered. Analysis of the filtrate

gave a Mg:Cl ratio of 1.0:0.15. The infrared spectrum of the solution gave bands at 2175 and 2380 cm^{-1}.

Reaction of Sodium Borohydride and Chloromagnesium Aluminum Hydride in Tetrahydrofuran. - To 75 ml of chloromagnesium aluminum hydride in THF (0.2.056 m) was added 0.8348 gm of sodium borohydride. The solution was stirred for two days. The solution was filtered and the analysis of the filtrate gave a Mg:Al:Cl ratio of 2.43:1.0:0.3. The infrared spectrum of the solution showed bands at 2380 cm^{-1}, 2175 cm^{-1} and 1725 cm^{-1}, 755 cm^{-1} and 795 cm^{-1}. 2.8591 gm of solid were recovered. Analysis of the solid gave a Mg:Al:Cl:H ratio of 1.0:1.75:2.11:10. The infrared spectrum of the solid showed a band at 1725 cm^{-1}.

Reaction of Sodium Aluminum Hydride and Chloromagnesium Borohydride in Tetrahydrofuran. - To 50 ml of chloromagnesium borohydride in THF (0.4887 m) was added 20.72 ml of sodium aluminum hydride (1.179 m) in THF. The solution was stirred over night. The solution was filtered and the analysis of the filtrate gave a Mg:Al:Cl ratio of 1.0:0.37:0.26. The infrared spectrum of the solution gave bands at 2380 cm^{-1}, 2175 cm^{-1}, 1720 cm^{-1}, 795 cm^{-1} and 755 cm^{-1}. A white solid from the filtration gave on analysis a Mg:Al:Cl ratio of 1.0:1.55:1.88. The infrared spectrum of the solid gave bands at 1725 cm^{-1}, 1025 cm^{-1}, 870 cm^{-1}, 795 cm^{-1} and 745 cm^{-1}.

Reaction of Magnesium Borohydride and Magnesium Aluminum Hydride in Tetrahydrofuran. - To 20 ml of magnesium borohydride in THF (0.34 m) was added 1.8843 gm of $Mg(AlH_4)_2 \cdot 4THF$ and the solution was stirred for two days. The infrared spectrum of the solution showed bands at 2380 cm^{-1} and 2175 cm^{-1} with a weak band at 1720 cm^{-1}.

Reaction of Magnesium Borohydride and Magnesium Aluminum Hydride in Benzene. - To 25 ml of magnesium borohydride as the THF etherate in benzene (0.34 M) was added 1.8474 gm of $Mg(AlH_4)_2 \cdot 4THF$. The solution was stirred for two days. The infrared spectrum of the solution showed bands at 2380 cm^{-1} and 2175 cm^{-1}.

Reaction of Tri-n-octyl-n-propyl Ammonium Aluminum Hydride and Magnesium Aluminum Hydride in Tetrahydrofuran. - To 65.82 ml of $n\text{-}Oct_3\text{-}n\text{-}PrNAlH_4$ (0.1353 m) was added 3.3335 gm of $Mg(AlH_4)_2 \cdot 4THF$. The solution was stirred for two days and filtered. Analysis of the filtrate showed no magnesium in solution. The infrared spectrum of the filtrate was unchanged from the original solution. The analysis of the solid obtained from the filtration gave a Mg:Al ratio of 1.0:1.96.

Reaction of Tri-n-Octyl-n-Propyl Ammonium Aluminum Hydride and Magnesium Aluminum Hydride in Benzene. - To 2.0560 gm of magnesium aluminum hydride was added 75 ml of $n\text{-}Oct_3\text{-}n\text{-}PrNAlH_4$ in benzene (0.2 m). The solution was stirred for two days at room temperature. After this time the infrared spectrum of the solution was the same as it was at the start of the reaction. The solution was then refluxed over night. The infrared spectrum was still not changed. The solution was now filtered and the filtrate was shown by analysis not to contain magnesium. From the filtration was isolated 0.1309 gm of solid. The infrared spectrum of this solid show no bands corresponding to Al-H but do have broad bands resembling magnesium hydride. The X-ray powder pattern of the solid showed lines due to magnesium hydride.

Results and Discussion

The compound chloromagnesium aluminum hydride obtained from previous work[2] seemed the obvious precursor to the compound $Mg(AlH_4)(BH_4)$. Therefore to a THF

solution of $ClMgAlH_4$ was added $NaBH_4$ in one to one stoichiometry.

$$NaBH_4 + ClMgAlH_4 \not\rightarrow BH_4MgAlH_4 + NaCl \qquad (1)$$

A white solid was obtained from this reaction which proved to be a mixture of sodium chloride and magnesium aluminum hydride. The infrared spectrum and elemental analysis showed that the solution contained magnesium borohydride.

Chloromagnesium borohydride has been found to be monomeric in refluxing THF.[6] If we assume that it is still monomeric at 25°C then the addition of sodium aluminum hydride to chloromagnesium borohydride should yield $Mg(AlH_4)(BH_4)$.

$$ClMgBH_4 + NaAlH_4 \not\rightarrow BH_4MgAlH_4 + NaCl \qquad (2)$$

However this reaction afforded a solid containing sodium chloride and magnesium aluminum hydride leaving magnesium borohydride in solution. In a separate experiment magnesium aluminum hydride and magnesium borohydride which had been synthesized independently were found not to redistribute in either THF or benzene solution. It therefore seems reasonable to assume that $Mg(AlH_4)(BH_4)$ when formed disproportionates to magnesium aluminum hydride and magnesium borohydride.

$$2(BH_4MgAlH_4) \rightarrow Mg(BH_4)_2 + Mg(AlH_4)_2 \qquad (3)$$

In 1968 Rice and Ehrlich reported the preparation of lithium beryllium aluminum hydride [$LiBe(AlH_4)_3$] by the addition of excess lithium aluminum hydride to beryllium chloride. Triethylamine was then added and over a period of seven

days the $LiBe(AlH_4)_3$ precipitated from solution. In our studies[2] of the reaction of alkali metal aluminum hydrides with magnesium halides in ether solvents we examined the reactions where the alkalimetal aluminum hydride was added in excess. However, we were not able to isolate a complex of the type $MMg(AlH_4)_3$. Instead the solid product contained a physical mixture of the alkali metal halide and magnesium aluminum hydride and the excess alkali metal aluminum hydride remained in solution.

$$n(MAlH_4) + Mg(AlH_4)_2 \not\rightarrow M_nMg(AlH_4)_{2+n} \qquad (4)$$

It was thought that perhaps a large cation would stabilize the complex $[MMg(AlH_4)_3]$. Trioctylpropylammonium aluminum hydride therefore was mixed with magnesium aluminum hydride in THF. However, after stirring for several days only unreacted starting materials were recovered. A similar experiment was performed in benzene. This was stirred at room temperature for two days after which time no reaction was detected. The solution was then refluxed over night. No magnesium was detected in solution however the weight of the solid had been reduced considerably. The infrared spectrum of the solid showed no bands in the Al-H stretching region. Instead it corresponded to a spectrum of magnesium hydride. The X-ray powder pattern of the solid confirmed this and showed lines corresponding to magnesium hydride. The infrared spectrum of the final solution was however unchanged from that of the original solution of the trioctylpropylammonium aluminum hydride. We are currently continuing the study of this reaction.

$$NR_4AlH_4 + Mg(AlH_4)_2\downarrow \rightarrow MgH_2\downarrow + NR_4AlH_4 \cdot 2AlH_3 \ (?) \qquad (5)$$

Concerning the Preparation of Beryllium Aluminum Hydride. A Study of the Reactions of Lithium Aluminum Hydride and Sodium Hydride with Beryllium Chloride in Diethyl Ether and Tetrahydrofuran.

R. Sanders and E. C. Ashby

Abstract

Contrary to previous reports beryllium aluminum hydride [$Be(AlH_4)_2$] could not be prepared from the reaction of either sodium- or lithium aluminum hydride with beryllium chloride in diethyl ether or tetrahydrofuran. Lithium aluminum hydride and $BeCl_2$ in 2:1 ratio were found to react in diethyl ether according to equation (1).

$$2LiAlH_4 + BeCl_2 \rightarrow BeH_2\downarrow + 2LiCl\downarrow + 2AlH_3 \qquad (1)$$

In 1:1 ratio in diethyl ether, evidence has been found for the reaction scheme shown in equations (2) and (3).

$$LiAlH_4 + BeCl_2 \rightarrow 1/2\ BeH_2\downarrow + LiCl\downarrow + AlH_3 + 1/2\ BeCl_2 \qquad (2)$$

$$BeCl_2 + AlH_3 \rightarrow HBeCl + ClAlH_2 \qquad (3)$$

In tetrahydrofuran, both $LiAlH_4$ and $NaAlH_4$, in 2:1 ratio with $BeCl_2$, appear to react according to equations (4) and (5). No evidence for $Be(AlH_4)_2$ as an initial product was found. The insoluble BeH_2 product of equation (4) was partially dissolved on prolonged stirring of the solution; however, the soluble

$$2NaAlH_4 + BeCl_2 \rightarrow AlH_3 + BeH_2\downarrow + 2NaCl\downarrow \quad (4)$$

$$2LiAlH_4 + BeCl_2 \rightarrow AlH_3 + [2LiCl \cdot BeH_2] \quad (5)$$

product was contaminated by tetrahydrofuran cleavage products. The data for reactions of $LiAlH_4$ or $NaAlH_4$ with $BeCl_2$ in 1:1 ratio in tetrahydrofuran support the descriptions shown in equations (6) and (7).

$$LiAlH_4 + BeCl_2 \rightarrow AlH_3 + HBeCl + LiCl \quad (6)$$

$$NaAlH_4 + BeCl_2 \rightarrow AlH_3 + HBeCl + NaCl\downarrow \quad (7)$$

Introduction

There is very little published literature which defines the products of the reaction of complex metal hydrides of aluminum such as $LiAlH_4$ or $NaAlH_4$ with beryllium halides in ether solvents. In 1951 Wiberg and Bauer[1] reported

(1) E. Wiberg, R. Bauer, Z. Naturf., 6b, 171 (1951).

that the reaction of $LiAlH_4$ with $BeCl_2$ in diethyl ether proceeds as shown in equation (8) to yield beryllium aluminum hydride $Be(AlH_4)_2$ and LiCl. The insoluble LiCl was reported to precipitate from solution leaving dissolved $Be(AlH_4)_2$ which was recovered by removal of solvent.

$$2LiAlH_4 + BeCl_2 \rightarrow Be(AlH_4)_2 + 2LiCl\downarrow \quad (8)$$

Wood and Brenner[2] reported that metastable solutions of $Be(AlH_4)_2$

(2) G. B. Wood, A. Brenner, J. Electrochem. Soc., 104, 29 (1957).

could be prepared by combining $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in diethyl ether. It was reported that a white precipitate formed and was filtered from the solution leaving a filtrate having the elemental analysis, Be/Al/H = 1.0/1.82/9.2, indicating the presence of $Be(AlH_4)_2$ in solution. The product was said to decompose within a few hours at the boiling point of ether; however, it was stable for several days at temperatures below 10°C. The solution could be stabilized by the addition of $BeCl_2$ or $AlCl_3$. The absence of data other than analysis leaves this product poorly described. The decomposition products were not characterized.

In other work[3], the reaction of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio in diethyl ether has been shown to yield a precipitate of LiCl and BeH_2, leaving AlH_3 in solution.

(3) C. E. Holley, J. F. Lemons, The Preparation of the Hydrides of Magnesium and Beryllium, Los Alamos Scientific Laboratory Report, LA-1660, April 1, 1954.

Related to the work above is the reported preparation of $LiBe(AlH_4)_3$ which has been described in a recent patent.[4] This compound was prepared by

(4) G. Rice, R. Ehrlich, U. S. Patent 3,383,187, May 14, 1963.

the addition of $LiAlH_4$ in diethyl ether to a slurry of $BeCl_2$ in a mixture of

ether and hexane, at room temperature, in 2:1 ratio. Immediate precipitation resulted and the precipitated solid was removed as soon as the combination of reagents was completed. After addition of triethylamine to the filtrate, a solid having the empirical formula $LiBe(AlH_4)_3$ precipitated over a period of seven days. The yield was ca. 5 per cent based on $BeCl_2$. The compound was characterized by elemental analysis and characteristic X-ray powder diffraction pattern. An explanation of the results claimed in this work may be formulated (equation 9) based on the results reported in prior art. If $Be(AlH_4)_2$ were

$$4LiAlH_4 + 2BeCl_2 \rightarrow [Be(AlH_4)_2 + BeCl_2 + 2LiAlH_4 + 2LiCl] \qquad (9)$$

$$\rightarrow LiBe(AlH_4)_3 + 1/2\ BeH_2\downarrow + AlH_3 + 1/2\ BeCl_2 + 3LiCl\downarrow$$

formed initially and reacted preferentially with the $LiAlH_4$ reactant to form a stable adduct, the complex might be isolated after removal of the insoluble products. The addition of triethylamine to the product solution may serve to prevent disproportionation of the complex, or to induce precipitation of the complex.

As can be seen from the literature cited above, there are conflicting descriptions of the reaction of $LiAlH_4$ and $BeCl_2$ in ether solvents. From analogous studies[5] of reactions of $LiAlH_4$ and $NaAlH_4$ with MgX_2 (X = Cl, Br, I)

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(5) E. C. Ashby, R. D. Schwartz, B. D. James, Inorg. Chem., 9, 325 (1970).

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in diethyl ether and tetrahydrofuran, it was found that halogen atoms were replaced in a stepwise fashion in a simple metathetical exchange process to yield

$XMgAlH_4$ and/or $Mg(AlH_4)_2$. The nature of the products was controlled by the choice of halogen and the solvent type. Reaction of zinc,[6] cadmium,[7] and mercury[7]

(6) E. Wiberg, W. Henle, R. Bauer, Zeit. Naturf., 6b, 393 (1951) and 7b, 249 (1952).

(7) E. Wiberg, W. Henle, Zeit. Naturf., 6b, 461 (1951).

halides with $LiAlH_4$ in diethyl ether or tetrahydrofuran produced only the insoluble, unstable binary hydrides ZnH_2, CdH_2, HgH_2 which decomposed to the metal and hydrogen gas at or below room temperature. Aluminum hydride was left in solution and it was postulated that $M(AlH_4)_2$ was formed as an intermediate, which then rapidly decomposed according to equation (10). The reaction of $NaAlH_4$ and $CaCl_2$ in 2:1 ratio is reported to yield $Ca(AlH_4)_2$ and NaCl.[8]

$$M(AlH_4)_2 \rightarrow MH_2 + AlH_3 \quad (M = Zn, Cd) \qquad (10)$$

(8) British Patent, 905,985 (1962).

Recent Russian work[9] has reported the preparation of $LiAl_2H_7$ and $LiAl_3H_{10}$

(9) T. N. Dymova, et al., Dokl. Akad. Nauk SSSR, 184 (6), 1338 (1969).

in diethyl ether according to the stoichiometries shown in equations (11) and (12).

$$2\ LiAlH_4 + BeCl_2 \rightarrow LiAl_2H_7 + HBeCl + LiCl \qquad (11)$$

$$3\ LiAlH_4 + BeCl_2 \rightarrow LiAl_3H_{10} + BeH_2 + 2LiCl \qquad (12)$$

The compounds $LiAl_2H_7$ and $LiAl_3H_{10}$ were reported to be very unstable in ether but somewhat more stable in the solid state as crystals.

Since the published data are in disagreement concerning the course of the reaction when $LiAlH_4$ and $BeCl_2$ are combined in diethyl ether, this reaction was reexamined in an attempt to clarify the conflicting reports. The reaction of $LiAlH_4$ and $NaAlH_4$ with $BeCl_2$ in tetrahydrofuran solvent was also studied. Using elemental analysis, infrared spectroscopy, and X-ray powder diffraction techniques the above systems were studied in an attempt to characterize the reaction products.

Experimental Section

Reagents

Beryllium metal was obtained from the Brush Beryllium Company, Elmore, Ohio. The metal was in the form of high purity electrorefined flake. Purity assay is given in Part I.

Chlorine gas was Matheson high purity, used without further purification.

All solvents were distilled at atmospheric pressure from $LiAlH_4$ (diethyl ether) or $NaAlH_4$ (benzene, tetrahydrofuran) immediately before use.

$LiAlH_4$ and $NaAlH_4$ were obtained as gray, lumpy solids from Ventron, Metal Hydrides Division.

Analytical

Aluminum was determined by a back-titration method at pH 4 using dithizone (diphenylthiocarbazone) as the indicator. To the sample was added 10 per cent excess standard EDTA solution, followed by adjustment of pH using dilute (1:1) ammonium hydroxide until the solution was just alkaline to methyl red. The

solution was then boiled for two minutes, cooled to room temperature or below, and approximately 10 ml of pH 4 buffer was added. Ethanol was then added to give ca. 40-50 per cent, by volume, ethanol. After dithizone indicator was added, the sample was titrated with standard zinc acetate solution to an equivalence point signified by a color change from blue-green to pink. Beryllium in equimolar amounts does not interfere.

Beryllium was determined gravimetrically by precipitation as the hydroxide, followed by ignition to the oxide at 1060°C for one hour.[8] Aluminum interference was prevented by the addition of an excess of EDTA which complexes the aluminum and prevents its precipitation as the hydroxide.

Analysis for chloride was done using the modified Volhard procedure. Chloride was precipitated as AgCl by the addition of excess standard $AgNO_3$. Benzyl alcohol was added to coat the halide precipitate and the solution was back-titrated with standard KCNS using ferric ion as the indicator.

Hydrogen analysis was accomplished by acid hydrolysis of a weighed amount of sample and collecting the evolved gas in a calibrated gas buret. Hydrolysis was carried out in an organic diluent (diglyme or benzene) to moderate the reaction. A dry ice trap prevented any condensable vapor from entering the measuring volume.

Preparative Methods

All operations were carried out under an atmosphere of dry, oxygen-free nitrogen in the dry box or using bench-top inert atmosphere techniques.[10]

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(10) D. F. Shriver, The Manipulation of Air Sensitive Compounds, McGraw-Hill Book Co., New York, 1969, Chapter 7.

Standard Solutions of Complex Aluminum Hydrides

Solutions of $LiAlH_4$ in diethyl ether and tetrahydrofuran and solutions of $NaAlH_4$ in tetrahydrofuran were prepared by stirring the solid hydride for 24 hours with the appropriate solvent, followed by filtration, to yield a clear, colorless solution. These reactant solutions were standardized by aluminum analysis and [illegible] volumetrically.

Beryllium Chloride

Beryllium chloride was prepared using a hot tube reaction described earlier.[11] Argon was used as a carrier gas instead of nitrogen, resulting in an almost quantitative yield of $BeCl_2$. To prepare the etherates of $BeCl_2$, a quantity of the unsolvated halide was suspended in dry benzene and the mixture cooled in an ice-water bath. A quantity (50 per cent excess based on the bis-solvate) of dry diethyl ether or tetrahydrofuran was added slowly as the mixture was stirred. The solvated, crystalline $BeCl_2$ was recovered by filtration and dried at reduced pressure. Analysis for $BeCl_2 \cdot 2THF$ gave the following results: Be- found 3.93%, calc. 4.02%; Cl- found 30.9%, calc. 31.6%. For $BeCl_2 \cdot 2Et_2O$ the results were: Be- found 3.86%, calc. 3.9%; Cl- found 30.5%, calc. 31.1%. Infrared and X-ray powder diffraction data were recorded.

$LiAlH_4 + BeCl_2$ in 2:1 Ratio in Diethyl Ether

To 32.29 mmoles of $BeCl_2$ in 250 ml of diethyl ether was added 64.58 mmoles of $LiAlH_4$ solution. The solution was cooled in an ice-water bath as the hydride addition was made. A white precipitate formed at once and increased in volume

(11) J. R. Sanders and E. C. Ashby, J. Am. Chem. Soc., 90, 6385 (1968).

as more $LiAlH_4$ was added. The mixture was stirred for 15 hours and filtered through a glass frit, yielding a white residue and a colorless, clear filtrate. Removal of solvent from the filtrate yielded a white powder.

Analysis of the insoluble residue indicated the following: H- 2.6%, Be- 7.72%, Al- 6.43%, Cl- 60.6%. The X-ray powder diffraction pattern contained only lines arising from LiCl. The infrared spectrum (nujol mull) exhibited very bored absorptions at 1755, ca. 1350, and 765 cm^{-1}.

Analysis of the ether-soluble fraction gave the following results: H- 5.99%, Li- 0.73%, Al- 30.2%; no beryllium or chloride was recovered in this material. The powder diffraction pattern contained no lines attributable to LiCl or starting materials. The infrared spectrum of a nujol mull of this material showed the following absorptions: 1755 (s,v.br.), 1660 (s,v.br.), 1022 (s), 720 (s,br.), 605 (m).

A similar experiment was performed at -78°C, stirred at this temperature for 60 minutes and filtered in the cold. Again, a white residue was recovered, leaving a clear, colorless filtrate. Analysis of the insoluble residue gave the following results: H-2.40%, Be-7.50%, Al-8.55%, Cl-60.6%. The infrared spectrum of a nujol mull of the insoluble residue gave the following absorptions: 1750 (s,v.br.), 1350 (s,v.br.), 765 (m,v.br.), 316 (s,br.). The X-ray powder diffraction pattern indicated no lines other than those arising from LiCl. The solid isolated by removing solvent from the ether-soluble fraction of this reaction gave the analysis: H-5.90%, Li-0.78%, Al-30.2%, again, no beryllium or halogen was found. The infrared spectrum had absorptions at: 1770 (s,v.br.), 1600 (s,v.br.), 1020 (s,br.), 720 (s,br.), 577 (s,br.). The X-ray powder diffraction pattern

showed no lines attributable to LiCl or starting materials. Recovery of elements from these reactions averaged 85 to 90 per cent.

Equilibration of a 2:1 mixture of $LiAlH_4$ and $BeCl_2$ in diethyl ether for 13½ hours at 25°C yielded products with infrared spectra identical to the products isolated when the reaction mixture was worked up immediately. The X-ray powder pattern of the insoluble product exhibited only lines of LiCl.

NaAlH$_4$ + BeCl$_2$ in 2:1 Ratio in Tetrahydrofuran

To a stirred suspension of 20.8[illegible] mmoles of $BeCl_2 \cdot 2THF$ in 150 ml of tetrahydrofuran, cooled to 0°C in an ice-water bath, was added 42.[illegible] mmoles of $NaAlH_4$ solution. An immediate precipitation resulted. After stirring for 30 minutes at 0°C, the mixture was filtered in the cold yielding a white residue and clear, colorless filtrate. Removal of tetrahydrofuran from this filtrate at reduced pressure produced a white solid.

Analysis of the insoluble fraction of this reaction indicated the following composition: H-1.36%, Be-3.61%, Al-1.91%, Cl-46.9%. The X-ray powder diffraction pattern of this sample contains five unidentified lines in addition to those arising from NaCl. The infrared spectrum of a nujol mull of this sample exhibited the following absorptions: 1710 (s,v.br.), 1350 (s,v.br.), 1020 (w), 815 (s,v.br.).

Analysis of the residue from the soluble fraction of this reaction shows the composition: H-3.0%, Be-0.309%, Al-26.2%, Cl-0.763%. The X-ray powder diffraction pattern of this sample had many lines, but none due to $BeCl_2 \cdot 2THF$. The infrared spectrum of a nujol mull shows absorptions at the following positions: 1800 (s,br.), 1625 (m,v.br.), 1015 (s,br.).

This reaction was repeated and the products stirred together at room temperature for a period of time to allow possible product redistribution. To 10.39 mmoles of $BeCl_2 \cdot 2THF$ in 70 ml of tetrahydrofuran was added 20.77 mmoles of $NaAlH_4$. The reaction was initiated at room temperature, producing an immediate white precipitate, and the mixture was stirred for 92 hours. At the end of the equilibration period, no obvious further solubilization had occurred and the mixture consisted of a fine white solid suspension. Filtration of this mixture produced a white residue and a colorless filtrate. Infrared examination of the filtrate showed the following absorptions (THF bands deleted): 1640 (s), 793 (s), 726 (s). Nmr spectra of the filtrate indicated nothing other than solvent over a 950 cps sweep width. Removal of solvent from this filtrate yielded a white solid whose analysis was: H-3.39%, Be-3.70%, Al-25.6%, Cl-2.59%. A nujol mull of this solid had absorptions in the infrared at: 1816 (s,br.), 1606 (s,v.br.), 1350 (m,br.), 1170 (w), 1120 (w), 1017 (w), 969 (w), 846 (w), 740 (m,br.), 671 (w). The X-ray powder diffraction pattern of this solid consists of four lines also found in the product resulting by removing solvent from the reaction mixture $2LiAlH_4 + BeCl_2$ in tetrahydrofuran.

The insoluble residue of this reaction had the analysis: H-0.649%, Be-2.77%, Al-1.80%, Cl-44.2%. The infrared spectrum of a nujol mull of this solid had the following absorptions: 1805 (s,br.), 1683 (s,br.), 1544 (s,br.), 1322 (m,sh), 1238 (w), 1150 (m), 1058 (m,sh), 1029 (s), 986 (m), 967 (m), 855 (s,br.), 764 (s,br.), 723 (s,br.). The X-ray powder diffraction pattern contains the NaCl pattern plus a faint, indistinct line found in the pattern observed above for the soluble portion.

An attempt was made to detect the presence of butoxy-alane species in the soluble 2:1 product which had been equilibrated for 92 hours. Acid hydrolysis of the solid, followed by benzene extraction, of the hydrolysate, confirmed the presence of 1-butanol when the extract was examined by vapor phase chromatography. The estimated aluminum/butanol ratio was slightly greater than one.

$LiAlH_4$ + $BeCl_2$ in 2:1 ratio in Tetrahydrofuran

To 32.1 mmoles of $BeCl_2 \cdot 2THF$ suspended in 200 ml of dry tetrahydrofuran was added 64.2 mmoles of $LiAlH_4$. No heat of reaction was noted, but most of the suspended halide dissolved immediately leaving a slightly turbid solution. Stirring at 25°C for 48 hours produced a completely clear, colorless, homogeneous solution. Removal of solvent until the volume was 100 ml caused no change. Approximately 100 ml of dry benzene was distilled into the solution, causing the appearance of a white precipitate. After removal of 50 ml of solvent by reduced pressure distillation, the solution was filtered to separate the white insoluble residue from the clear filtrate. The residue was shown to be pure LiCl (26 mmoles) by infrared and powder diffraction examination. Evaporation of the remainder of the solvent produced a gummy residue which solidified. The X-ray powder diffraction pattern of this solid showed the presence of additional LiCl plus nine other weak lines which could have arisen from a trace of $BeCl_2 \cdot 2THF$ or $LiAlH_4 \cdot nTHF$. The infrared spectrum of a nujol mull of this material showed the following absorption patterns: 1802 (s), 1023 (m), 842 (m), 752 (s), 725 (s), 623 (w), 528 (w).

Readdition of 100 ml of benzene to the product, followed by vigorous stirring, caused dissolution of some of the solid material. Filtration yielded

a white residue and a colorless filtrate. The X-ray powder diffraction pattern of the white solid indicated the presence of LiCl plus lines found in the original sample before benzene addition. The infrared spectrum of this solid has the following absorptions: 1812 (s,br.), 1616 (s,v.br.), 1236 (m,br.), 1071 (m), 1028 (m), 859 (m), 843 (m), 753 (s), 605 (s), 534 (s). Removal of benzene solvent from the filtrate produces a gummy solid which would not solidify after prolonged pumping at 10^{-5} mm pressure, and for which no diffraction data could be obtained. The infrared spectrum of a nujol mull of this material was the same as that found for the original material before benzene addition, with the appearance of a broad band of low intensity at 1619 cm^{-1}.

Analysis of the benzene-insoluble portion of this reaction gave the following values: H-1.86%, Al-17.0%, Cl-37.4%. Analysis of the benzene-soluble product indicated the composition: H-1.68%, Be-4.47%, Al-16.6%, Cl-1.88%.

The 2:1 reaction between $LiAlH_4$ and $BeCl_2$ in tetrahydrofuran was repeated under conditions designed to minimize solvent cleavage. To 12.37 mmoles of $BeCl_2 \cdot 2THF$ was added 24.74 mmoles of $LiAlH_4$ in 225 ml of tetrahydrofuran. The reaction mixture temperature was maintained at 0°C with vigorous stirring for 15 hours, producing a slightly turbid solution. The turbidity vanished when the mixture was stirred at room temperature for two hours. Solvent was removed by reduced pressure distillation at low temperature. The solution remained clear until a volume of 30 ml was reached, where a steadily increasing amount of solid began to precipitate. The final product was a white solid and was evacuated for 12 hours to remove excess solvent. The infrared spectrum of a nujol mull of this material had the following absorptions: 1808 (s,br.), 1616 (m,v.br.), 1017 (s), 852 (m), 730 (m), 621 (m). The X-ray powder pattern of this solid contains LiCl

lines plus other well-defined lines which match the corresponding sample from the previous reaction, with the exception of four weak lines.

The reaction in the preceding paragraph was repeated and the residue isolated by solvent removal was extracted with benzene at room temperature for one hour. A white suspension resulted and filtration produced a white residue and a clear filtrate. The infrared spectrum of the insoluble residue exhibited the following absorptions: 1765 (s,br.), 1350 (m,br.), 1007 (w), 841 (w,br.), 1718 (w), 669 (s), 400-200 (s,br.). Evaporation of benzene from the filtrate produced a white solid with the following analysis: H-3.19%; Al-28.5%; Cl-5.22%, beryllium concentration was too small to measure accurately; no lithium was found by flame photometric analysis. The infrared spectrum of this product had the following absorptions: broad strong absorption from 2000 to 1300 cm^{-1}; 1169 (w), 1079 (m), 910 (w), 716 (w), 669 (w), 246 (m).

<u>$LiAlH_4$ + $BeCl_2$ in 1:1 Ratio in Tetrahydrofuran</u>

$LiAlH_4$ (28.9 mmoles) was added dropwise to a stirred suspension of 28.9 mmoles of $BeCl_2$ in 200 ml of tetrahydrofuran at 25°C. The suspended crystals of $BeCl_2 \cdot 2THF$ dissolved immediately, leaving a slightly turbid solution. Stirring for 15 hours yielded a perfectly clear, homogeneous solution. Distillation of 150 ml of benzene into the reaction mixture left it unchanged. Removal of solvent at reduced pressure until the total volume is approximately 20 ml caused the appearance of a precipitate which was identified as LiCl upon isolation. The filtrate precipitated more LiCl on standing. Removal of the remainder of the solvent yielded a gummy solid which solidified after prolonged pumping at 0.5 mm pressure. The infrared spectrum of this solid had absorptions at: 1877 (m), 1802 (s), 1781 (s), 1618 (m,v.br.), 1238 (w), 1170 (w), 1115 (w), 1060 (m),

1028 (s), 967 (s), 916 (w), 875 (w), 754 (m), 657 (m), 580 (w), 460 (m). The X-ray powder pattern indicated the presence of LiCl plus many additional lines which did not match $BeCl_2 \cdot 2THF$.

The addition of 60 ml of dry benzene to this solid produced a white slurry which was stirred for several hours and filtered. The white residue obtained had the following infrared spectrum: 1880 (w,br.), 1830 (w,br.), 1539 (s,br.), 1189 (m,br.), 1122 (w), 1062 (m), 998 (w), 972 (w), 898 (m), 803 (w), 724 (s), 563 (s), 338 (w). The X-ray powder diffraction pattern indicated the presence of LiCl plus seven unidentified lines. Analysis of the solid indicated the composition: H-1.26%, Be-0.76%, Al-43.4%, Cl-35.42%. Removal of benzene from the filtrate yielded a gummy solid which would not solidify with prolonged pumping at reduced pressure with heating (65°C, 24 hours). Slight discoloration of the material was noted along with some gas evolution, and the product was finally characterized as a plastic mass. Analysis of this product gave the following values: H-0.716%, Be-4.70%, Al-10.2%, Cl-16.1%. The infrared spectrum of a nujol mull of this product before heating at reduced pressure was: 1876 (s), 1810 (s), 1780 (sh), 1312 (w), 1267 (w), 1240 (w), 1169 (m), 1153 (w), 1116 (m), 1060 (s), 1028 (s), 965 (w), 948 (w), 901 (w), 843 (w), 760 (w,br.), 722 (w,br.), 664 (w), 570 (w,sh), 463 (s). The infrared spectrum of a nujol mull of the same sample after heating and evacuation shows the following absorptions: 1876 (s,br.), 1803 (s,sh), 1346 (w), 1306 (w), 1258 (m), 1238 (m), 1166 (s), 1114 (m), 1056 (s), 1023 (s,br.), 959 (s,br), 898 (m), 826 (s,br), 642 (s,br), 575 (m,sh), 525 (m), 458 (s).

The reaction was repeated in tetrahydrofuran at 0°C using 8.46 mmoles of $BeCl_2$ and 8.46 mmoles of $LiAlH_4$ in 150 ml of tetrahydrofuran. The mixture was

stirred for 15 hours at 0°C yielding a slightly turbid solution. Removal of solvent at reduced pressure caused no solid precipitation until approximately 50% of the solvent had been removed. The final product of solvent removal was a gummy solid. Thirty-nine hours of pumping at reduced pressure (0.1 mm, 25°C) yielded a plastic solid whose infrared spectrum was: 1778 (vs,br), 1575 (sh), 1237 (m), 1170 (s), 1110 (w), 1005 (s), 960 (m), 920 (s), 840 (s,br.). Continued pumping (24 hours) finally yielded a white powder whose infrared spectrum as a nujol mull was the following: 1802 (s,br.), 1619 (s,br.), 457 (w), plus an irregular baseline which showed no definite absorptions. The powder diffraction pattern of this solid indicated the presence of LiCl plus 11 additional lines which do not match $BeCl_2 \cdot 2THF$.

$NaAlH_4$ + $BeCl_2$ in 1:1 Ratio in Tetrahydrofuran

To a stirred suspension of 15.6 mmoles of $BeCl_2 \cdot 2THF$ in 150 ml of tetrahydrofuran was added 15.6 mmoles of $NaAlH_4$. The reaction was cooled in an ice-water bath as the addition was made, and the mixture was stirred for 30 minutes prior to filtration. A white precipitate formed as the reagents were combined. Filtration produced a white solid residue and a clear filtrate. Removal of solvent from the filtrate by reduced pressure distillation, in the cold, gave a white solid.

Analysis of the insoluble product gave the following: H-0.806%, Be-2.94%, Al-1.28%, Cl-43.4%. The infrared spectrum of a nujol mull of the solid had absorptions at the following positions: 1729 (s,br.), 1350 (m,v.br.), 1011 (s), 955 (w), 912 (w), 863 (s), 730 (m,br.), 542 (m,br.). The X-ray powder diffraction pattern shows the presence of $BeCl_2 \cdot 2THF$ and NaCl with three unidentified weak lines. Analysis of the solid isolated from the soluble portion of the reaction

mixture indicated the following composition: H-2.72%, Be-4.08%, Al-21.2%, Cl-15.8%. The infrared spectrum of a nujol mull of this solid had the following absorptions: 1874 (s,br.), 1573 (s,v.br.), 1160 (m,br.), 1019 (s,br.), 950 (s,br.), 829 (s,br.), 712 (s,br.), 649 (s,br.), 452 (m,br.), 369 (w), 343 (w). The X-ray powder diffraction pattern of this solid does not confirm the presence of $BeCl_2 \cdot 2THF$ or NaCl, but has many lines.

$LiAlH_4$ + $BeCl_2$ in 1:1 Ratio in Diethyl Ether

$LiAlH_4$ (25.03 mmoles) was added dropwise to 25.03 mmoles of $BeCl_2$ in 250 ml of diethyl ether at 0°C. A precipitate formed immediately. Stirring for 18 hours produced a clear supernatant solution over a flocculent precipitate. Filtration yielded a white solid and a clear filtrate. Removal of solvent from the filtrate produced a clear glass puddle which disintegrated upon further evacuation to a powder having a crystalline appearance.

Analysis of the insoluble material from this reaction gave the following results: H-2.46%, Be-8.37%, Al-3.25%, Cl-62.2%. The powder diffraction pattern of the solid indicated the pattern of LiCl plus three additional weak lines. The infrared spectrum of a nujol mull of this solid had the following absorptions: 1758 (s,v.br.), 1350 (m,v.br.), 1022 (w), 778 (m,v.br.). Analysis of the soluble product indicated the composition: H-2.65%, Be-3.58%, Al-23.0%, Cl-26.1%. The infrared spectrum of a nujol mull of this product exhibits absorptions at: strong, broad band from 2200 to 1200 cm^{-1}, 1190 (w), 1150 (w), 1091 (w), 1023 (w), 973 (w), 890 (w), 844 (w), 760 (w), 600 (w,br.), 444 (w). The X-ray powder pattern consisted of four diffuse lines which match those found for the 2:1 case, soluble species.

The reaction was repeated at -78° C using 22.7 mmoles of $BeCl_2 \cdot 2Et_2O$ and 22.7 mmoles of $LiAlH_4$ in 200 ml of diethyl ether. Again a precipitate formed immediately. After stirring for 45 minutes, filtration in the cold produced a white solid and a clear filtrate. Removal of the solvent from the filtrate produced a white solid.

Analysis of the insoluble residue gave the following composition: H-2.08%, Be-9.03%, Al-3.46%, Cl-56.1%. The infrared spectrum of a nujol mull of the insoluble solid had the following absorptions: 1765 (s,v.br.), 1350 (m,v.br.), 1190 (w), 1150 (w), 1085 (w), 1017 (m), 890 (w), 841 (w), 773 (m). The X-ray powder pattern showed the LiCl pattern plus one weak, unidentified line. The solid isolated from the soluble portion of this reaction mixture gave the analysis: H-3.25%, Be-1.08%, Al-28.2%, Cl-24.0%. The infrared spectrum of a nujol mull of this solid exhibited absorptions at: 1851 (m,v.br.), 1615 (m,v.br.), 1257 (w), 1187 (w), 1145 (w), 1086 (w), 1014 (w), 968 (w), 888 (w), 730 (m,br.), 620 (w), 443 (w). The X-ray powder diffraction pattern contains four weak lines.

Solution Spectra: $LiAlH_4$ - $BeCl_2$ in Diethyl Ether

Molar increments of $LiAlH_4$ were added to 9.23 mmoles of $BeCl_2$ dissolved in 50 ml of diethyl ether. After the hydride addition, the mixture was stirred for 30 minutes to 1 hour, the precipitate allowed to settle, and samples (1 ml) of the clear supernatant were withdrawn by syringe for infrared examination. Absorptions at 1:1 = hydride halide ratio were: (solvent bands omitted) 1848 (s), 1787 (s), 1638 (w), 964 (m), 904 (m), 784 (s), 712 (s), 569 (w), 502 (w). These bands were unchanged on stirring for 16 hours. Absorptions at 2:1 ratio were

1811 (s,sh.), 1787 (s), 1638 (w), 900 (w), 753 (s), 675 (m), 540 (w). Absorptions at 3:1 ratio were: 1812 (s,sh.), 1785 (s), 1747 (s), 900 (w), 754 (s), 685 (m), 540 (w). Filtration of the mixture produced a white residue which had the following spectrum after drying at reduced pressure: 1754 (s,br.), 1350 (m,br.), 1025 (w), 752 (s,br.). The powder diffraction pattern of this solid showed only LiCl and a single additional, indistinct line. Removal of ether from the clear, colorless filtrate produced a white solid having the infrared spectrum: 1778 (s,br.), 1618 (s,br.), 1147 (w), 1026 (s), 891 (m,sh.), 802 (w,sh.), 720 (s,br.), 600 (s). The X-ray powder diffraction pattern of this solid contained eight lines. A sample of $LiAlH_4$ solution was stripped of solvent at 25°C to yield a white solid whose infrared spectrum was: 1778 (s,br.), 1666 (s,br.), 1148 (w), 867 (s,br.), 714 (s,br.). The X-ray powder pattern of this partially desolvated hydride did not match the pattern for the ether-soluble product described above. The soluble reaction product was unstable and decomposed to a dark gray solid with gas evolution.

Solution Spectra: $LiAlH_4$ + $BeCl_2$ in Tetrahydrofuran

$LiAlH_4$ solution was added to 4.54 mmoles of $BeCl_2$ in 50 ml of tetrahydrofuran. Spectra were recorded from samples of the clear, homogeneous solution. Absorptions at 0:1 ratio: 665 (s,sh.), 574 (m), 524 (w). Absorptions at 1:1 ratio: 1730 (s,br.), 773 (m), 729 (m), 670 (s,sh.), 378 (w). Absorptions at 2:1 ratio: 1730 (s,sh.), 1701 (s), 776 (s), 731 (w), 680 (m,sh.), 370 (m,br.). Absorptions at 3:1 ratio: 1730 (s,sh.), 1695 (s), 1646 (m,sh.), 774 (s), 731 (w), 680 (m,sh.), 370 (m,br.). Absorptions at 7:1 ratio: 1691 (s), 1646 (s,sh.), 763 (s), 733 (m,sh.), 679 (m), 530 (w), 384 (s). Absorptions of $LiAlH_4$ solution: 1691 (s), 763 (s), 390 (m).

Solution Spectra: $NaAlH_4$ + $BeCl_2$ in Tetrahydrofuran

The procedure was the same as above except that the precipitate formed would not settle on standing for one hour. At 2:1 ratio, the mixture was filtered and the infrared spectrum of the filtrate examined. Absorptions were found at: 1736 (s), 1269 (w,sh.), 797 (w), 724 (m). $NaAlH_4$ in tetrahydrofuran has absorptions at 1680 and 772 cm^{-1}.

Instrumentation

Infrared spectra were obtained on a Perkin-Elmer, Model 621, grating infrared spectrophotometer. Samples were prepared as nujol mulls or as ethereal solutions and were scanned from 2500 to 200 cm^{-1} using CsI cell windows.

Nmr spectra were recorded on a Varian Associates A60 nuclear magnetic resonance spectrometer (60 mc).

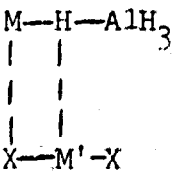
X-ray powder diffraction data were obtained using a Debye-Scherrer camera (Norelco, 114.6 mm) and Cu(Kα) radiation (1.5418 Å) with a nickel beta filter. Also, Mo(Kα) radiation (0.7107 Å) with a zirconium beta filter was employed. The samples were loaded into thin-walled Linnemann glass capillaries (0.5mm) in the dry box.

Results and Discussion

The reaction between complex aluminum hydrides $MAlH_4$ (where M = Li, Na, K, Cs) and metal halides of Group II, $M'X_2$ (where M' = Be, Mg, Ca, Zn, Cd, Hg; X = Cl, Br, I), may be described in two ways. The first of these descriptions would be the simple metathetical exchange shown in Equation 13. The complex aluminum hydride in this case is presumed to exist

$$2\ MAlH_4 + M'X_2 \rightarrow 2\ MX + M'(AlH_4)_2 \qquad (13)$$

as a solvent-separated ion pair. The second description employs a subtle difference in the constitution of the hydride reactant, i.e., the complex aluminum hydride may be thought of as an MH species coordinated to AlH_3 through a hydrogen bridge. Reaction of this bridged hydride species with $M'X_2$ might then occur by a different mechanism as shown in Equations 14 and 15, to form $M'H_2$ directly instead of $M'(AlH_4)_2$. Experimental verification of either of these two postulated processes is complicated by the possibility of a redistributio



$$\rightarrow XM'H + AlH_3 + MX \qquad (14)$$

$$XM'H + MAlH_4 \rightarrow M'H_2 + AlH_3 + MX \qquad (15)$$

disproportionation equilibrium (equation 16) which may be attained rapidly or very slowly.

$$M'(AlH_4)_2 \rightleftharpoons M'H_2 + 2\,AlH_3 \qquad (16)$$

The only alkali metal aluminum hydride which is soluble in diethyl ether is $LiAlH_4$. This unique behavior is attributed to strong solvation of the small lithium cation by the moderately basic ether. Where the cation is larger (Na or K) a more basic solvent, such as tetrahydrofuran, is required for solubilization. In the case of $CsAlH_4$, only a difunctional ether, such as diglyme, acts as a solvent. In general, it may be argued that solubility of these compounds is

dependent upon effective solvation of the cation and that for small cations a less basic solvent is required than for large cations. On the other hand, $(n\text{-}C_8H_{17})_3(n\text{-}C_3H_7)N]AlH_4$ is soluble in benzene[12] whereas $[(CH_3)_4N]AlH_4$ is not

(12) R. Ehrlich, A. R. Young, D. D. Perry, Inorg. Chem., 4, 758 (1965).

soluble in any organic solvents. The solubility of the former is probably due to the long alkyl chains on the ammonium cation; when such groups are absent, solubility is lost in hydrocarbon solvents due to poor solvation of the $(CH_3)_4N^+$ cation by benzene.

The infrared spectra of complex aluminum hydrides and other alane derivatives are complicated in some instances, but some useful, general statements can be made. Terminal Al-H stretching frequencies occur between 1912 cm^{-1} and 1660 cm^{-1}, and may be lower in bridging situations (1550 cm^{-1}). Deformation modes of AlH_4^- are observed at ca. 750 cm^{-1}. Shifts in Al-H stretching frequencies have been correlated with the increase or decrease of the coordination number of aluminum. In general, increasing coordination number for aluminum will cause the Al-H stretching frequency to decrease;[13] those compounds of coordination

(13) H. Roszinsky, R. Dautel, W. Zeil, Z. Physik. Chem., 36, 26 (1963).

number five absorb below 1790 cm^{-1} and those of coordination number four absorb above 1750 cm^{-1}. Dilts[14] has discussed the shift in the Al-H stretching frequency

(14) J. Dilts, E. C. Ashby, Submitted for publication.

in terms of covalent interactions for selected derivatives of complex aluminum hydrides.

Reactions in Diethyl Ether

Because of solubility, $LiAlH_4$ was the only hydride reacted with $BeCl_2$ in diethyl ether. Analytical data are summarized in Tables 1 and 2 for reactions at 25°C and -78°C.

The reactions of $LiAlH_4$ and $BeCl_2$ in 2:1 ratio are rapid and complete within one hour at -78°C. Aluminum hydride is recovered virtually uncontaminated, except by residual solvent, from the soluble fractions of the reaction mixture. The infrared spectrum of the reaction solution has a strong absorption at 1787 cm^{-1}, which does not agree closely with the value of 1801 cm^{-1} observed by Ehrlich[15] for a metastable alane solution prepared from $LiAlH_4$ and $AlCl_3$ using the method of Finholt, et al.[16] Aluminum hydride prepared in diethyl ether by this latter reaction precipitates from solution within minutes after its separation from the LiCl by-product. In contrast, the AlH_3 generated by $LiAlH_4$-$BeCl_2$ interaction is stable in solution over a period of at least 135 hours at room temperature. It appears that AlH_3 is being solubilized by the presence of solid LiCl or BeH_2

(15) R. Ehrlich, A. R. Young, B. M. Lichstein, D. D. Perry, Inorg. Chem., 2, 650 (1963).

(16) A. E. Finholt, A. C. Bond, H. I. Schlesinger, J. Am. Chem. Soc., 69, 1199 (1947).

Table 1. $LiAlH_4$ + $BeCl_2$ in Diethyl Ether at 25°

$LiAlH_4$:$BeCl_2$	Solubility of Product	H:Al	(Total H^- Less AlH_3):Be	Be:Cl
1:1	soluble	3.26:1.0	1.0:5.22	1.0:1.85
1:1	insoluble	20.2:1.0	2.24:1.0	1.0:1.89
2:1	soluble	3.12:1.0	no Be	no Be
2:1	insoluble	11.0:1.0	2.22:1.0	1.0:2.0

Table 2. $LiAlH_4$ + $BeCl_2$ in Diethyl Ether at -78°

$LiAlH_4$:$BeCl_2$	Solubility of Product	H:Al	(Total H^- Less AlH_3):Be	Be:Cl
1:1	soluble	3.09:1.0	1.0:2.22	1.0:2.04
1:1	insoluble	16.2:1.0	1.69:1.0	1.0:1.69
2:1	soluble	3.18:1.0	no Be	no Be
2:1	insoluble	10.3:1.0	2.06:1.0	1.0:2.05

according to an equilibrium of the type shown in equation (17). The infrared spectrum of the solid AlH_3 etherate which was isolated from the 2:1 reaction

$$\underset{\text{solid}}{L} + AlH_3 \rightleftharpoons [L{\cdot}AlH_3] \rightarrow AlH_3 + \underset{\text{solution}}{L}\downarrow \qquad (17)$$

(where L = LiCl, BeH_2)

had broad absorptions at 1755, 1660 cm^{-1} (25°) and 1778, 1600 cm^{-1} (-78°). The reported spectra[13] for $AlH_3{\cdot}xEt_2O$ show absorptions at 1760 and 1592 cm^{-1} as nujol mulls. The varying values of the absorption maxima arise from the extreme broadness of the bands and undoubtedly from slightly differing residual solvent content.

The insoluble products of the 2:1 reaction are LiCl and $BeH_2{\cdot}xEt_2O$. The infrared spectrum of the insoluble solid exhibits a strong, broad band at 1755 cm^{-1} (25°C) and 1750 cm^{-1} (-78°). The infrared spectrum of BeH_2 prepared by pyrolysis of $Be(BH_4)_2$ with $(C_6H_5)_3P$ in 2:1 ratio has a strong, broad Be-H stretching absorption at 1758 cm^{-1}; the product gave no X-ray powder diffraction pattern.[17] For the product isolated as the insoluble solid in the 2:1 reaction,

(17) L. Banford, G. E. Coates, J. Chem. Soc., 5591 (1964).

only lines arising from LiCl were noted in the X-ray powder diffraction pattern. Analytical data indicate a Be:H ratio of 1:2.

Thus, the original report by Wiberg[1] appears to be incorrect, and the work of Holley and Lemons[3] corroborated. The findings of Wood and Brenner[2] could not be substantiated since no $Be(AlH_4)_2$ was generated which could be stabilized at low temperatures. Also, we found no evidence for $LiBe(AlH_4)_3$

species[4] in reactions between $LiAlH_4$ and $BeCl_2$ in diethyl ether.

The Russian claim[9] concerning the preparation of $LiAl_2H_7$ could not be verified. Analysis of this new compound gave the elemental ratios: Li:Al:H = 1.0:2.19:7.0; the powder diffraction pattern was also reported. It is notable that the Al:H ratio of this product is only 1.0:3.2, and seems to be inconsistent with the reported empirical formula. We have found less than 0.8 per cent lithium in the soluble products of the 2:1 reaction of $LiAlH_4$ and $BeCl_2$ in diethyl ether and Al/Li ratio of approximately 17. X-ray powder diffraction data for these soluble products do not match those from the Russian report. The powder pattern of AlH_3 etherate which we have isolated from this 2:1 reaction at 25° does agree well with the powder pattern of an alane etherate reported by French workers[18] to

(18) J. Bousquet, J. Choury, P. Claudy, Bull. Soc. Chim. France, 3848 (1967).

be a limiting composition of desolvation efforts with $AlH_3 \cdot nEt_2O$.

For the reactions where the $LiAlH_4$:$BeCl_2$ ratio is 1:1, the reaction is more complex. The infrared data, elemental analysis, and X-ray powder diffraction pattern of the insoluble reaction product show that the major constituents are LiCl and BeH_2. Analysis of the soluble portion of the reaction indicates a mixture of AlH_3 and $BeCl_2$, but it is probable that such a mixture would react further according to equations (18) and (19).

$$AlH_3 + BeCl_2 \rightarrow H_2AlCl + HBeCl \qquad (18)$$

$$HBeCl + H_2AlCl \rightarrow HAlCl_2 + BeH_2\downarrow \qquad (19)$$

Such interactions would preserve the amount of soluble chloride and hydride if the hydridoberyllium compounds were either soluble or were complexed by the halogen-alane species which are soluble. Some support for AlH_3-$BeCl_2$ interactions is found in the infrared spectrum of the reaction solution itself, where a band at 1848 cm^{-1} is observed at 1:1 ratio only. The spectrum does not change after 16 hours of stirring. The triethylaminate of H_2AlCl is known to absorb at 1852 cm^{-1} in benzene, whereas the aminate of $HAlCl_2$ absorbs at 1898 cm^{-1}.[20] Thus, the most likely interaction would produce H_2AlCl and HBeCl, the

(20) E. C. Ashby, J. Prather, J. Am. Chem. Soc., 88, 729 (1966).

latter being an unreported compound.

Infrared data on solutions of $LiAlH_4$ and $BeCl_2$ where the ratio of these reactants is greater than 2:1 indicates only an increase in the absorption due to $LiAlH_4$.

Reactions in Tetrahydrofuran

Both $NaAlH_4$ and $LiAlH_4$ were allowed to react with $BeCl_2$ in tetrahydrofuran. Of the alkali halide by-products, NaCl is insoluble while LiCl is soluble.

The reaction of $LiAlH_4$ with $BeCl_2$ in both 1:1 and 2:1 ratios yields a mixture of products which are soluble. Fractional crystallization of the product solution deposited only pure LiCl; no evidence of BeH_2 deposition was observed. The infrared spectra of the product solutions exhibit an Al-H stretching band at 1730 cm^{-1} for a 1:1 ratio of reactants, 1701 cm^{-1} with a shoulder at 1730 cm^{-1} for 2:1 ratio, 1695 cm^{-1} with a shoulder at 1730 cm^{-1} for 3:1 ratio, and 1691 cm^{-1} at 7:1 ratio. $LiAlH_4$ in tetrahydrofuran absorbs at 1691 cm^{-1}. Aluminum hydride

in tetrahydrofuran solution is reported to absorb at 1739 cm^{-1} [21] and 1724 cm^{-1}.[15]

(21) R. Dautel, W. Zeil, Z. Electrochemie, 64, 1234 (1960).

The infrared spectrum of the product mixture after solvent removal exhibited Al-H stretching vibrations at 1808, 1616 cm^{-1} (2:1 mixture), and 1802, 1619 cm^{-1} (1:1 mixture). These are very close to the values expected for the tetrahydrofuranate of AlH_3 which absorbs at 1802 cm^{-1} [13] or 1810 cm^{-1}.[21] Thus, on the basis of the infrared data it is difficult to distinguish the reaction products from $AlH_3 \cdot xTHF$ since the bands are so broad. On the other hand, the fact that BeH_2 does not precipitate demonstrates clearly that a strong interaction is present. Since pure LiCl may be precipitated by the addition of a non-coordinating solvent such as benzene, the interaction products are suggested to be $Be(AlH_4)_2$ (2:1 reaction) or $ClBeAlH_4$ (1:1 reaction).

Using $NaAlH_4$ in tetrahydrofuran gives different results. The analytical data for reactions between $NaAlH_4$ and $BeCl_2$ in tetrahydrofuran are summarized in Tables 3 and 4.

At a $NaAlH_4$:$BeCl_2$ ratio of 2:1, the initial products are analogous to those found for the $LiAlH_4$:$BeCl_2$ = 2:1 reactions in diethyl ether. The soluble reaction product is predominantly $AlH_3 \cdot xTHF$, 3.1 is identified by its analysis and by the infrared spectrum which has strong hydridic absorptions at 1800 cm^{-1} and 1625 cm^{-1}. The insoluble reaction products are NaCl and BeH_2, the hydride Be-H stretching frequency being reduced to 1710 when the product is isolated from tetrahydrofuran. Stirring the 2:1 reaction mixture for 92 hours caused solubilization of the BeH_2 from the insoluble phase to the soluble portion of the reaction

Table 3. $NaAlH_4$ + $BeCl_2$ in Tetrahydrofuran (0°)

$NaAlH_4$:$BeCl_2$	Solubility of Product	H:Al	(Total H^- Less AlH_3):Be	Be:Cl
1:1	soluble	3.47:1.0	1.0:1.23	1.02:1.0
1:1	insoluble	16.9:1.0	1.0:1.23	1.0:1.52
2:1	soluble	3.14:1.0	1.0:1.23	8.40:1.0
2:1	insoluble	19.2:1.0	1.84:1.0	1.0:2.13

Table 4. $2NaAlH_4$ + $BeCl_2$ in Tetrahydrofuran (25°, 92 Hours)

$NaAlH_4$:$BeCl_2$	Solubility of Product	H:Al	(Total H^- Less AlH_3):Be	Be:Cl
2:1	soluble	3.57:1.0	1.32:1.0	5.62:1.0
2:1	insoluble	9.73:1.0	1.46:1.0	1.0:4.05

mixture. It is postulated that this interaction is of the type shown in equation (20). The infrared spectrum of the equilibrated solution had a

$$2AlH_3 + BeH_2 \rightarrow Be(AlH_4)_2 \qquad (20)$$

strong absorption at 1740 cm^{-1}, very close to the initial value of 1736 cm^{-1} which appears immediately after mixing. The solid obtained by removing solvent from this equilibrated solution exhibited Al-H stretching bands at 1816 cm^{-1} and 1606 cm^{-1}. This product is very similar to the soluble product from the 2:1 $LiAlH_4$ reaction, on the basis of infrared spectra and X-ray powder diffraction patterns.

The observation that the 2:1 reaction in tetrahydrofuran proceeds in a different manner for $LiAlH_4$ than for $NaAlH_4$ has two implications. The first consideration is the possibility that the compositions of these two hydrides are different in tetrahydrofuran solution and that each hydride species leads to a separate product mixture. The second possibility is that the LiCl by-product is able to solubilize BeH_2 readily whereas NaCl is ineffective in such a process.

The comparative degree of cation solvation should be the discriminating effect for these two hydrides in solution. The Al-H stretching vibrations for $LiAlH_4$ and $NaAlH_4$ in tetrahydrofuran solution are 1691 cm^{-1} and 1680 cm^{-1}, respectively. This is not a large change but indicates less cation-anion, covalent interaction when sodium is the cation. At the present time, little else is known about the composition of these hydrides in solution and it must

be concluded that there is no evidence for significant differences in these two reagents in tetrahydrofuran which would justify proposal of more than one reaction mechanism with $BeCl_2$.

On the other hand, LiCl is known to form soluble complexes with halogenalane species in diethyl ether[20] and evidence for $LiBr\text{-}AlH_3$ and $LiI\text{-}AlH_3$ adducts has been found in diethyl ether and tetrahydrofuran.[23,24] Therefore,

(23) H. Nöth, Dissertation, Univ. München, 1954.

(24) G. N. Schrauzer, Dissertation, Univ. München, 1956.

it is quite reasonable that LiCl would form a complex with BeH_2 and prevent its precipitation in the $LiAlH_4\text{-}BeCl_2$ reaction in tetrahydrofuran. This adduct could then react further with AlH_3 to produce $Be(AlH_4)_2$ as shown in equation (21).

$$LiBeH_2Cl + 2AlH_3 \rightarrow LiCl + Be(AlH_4)_2 \qquad (21)$$

$$(\text{or } Li_2BeH_2Cl_2)$$

When solvent is removed from a 2:1 mixture of $LiAlH_4$ and $BeCl_2$ in tetrahydrofuran, a white residue results. If this residue is extracted with benzene, the soluble product is solvated AlH_3 and not $Be(AlH_4)$. This result lends further support to the hypothesis that BeH_2 and AlH_3 are present in the solution, BeH_2 being solubilized by a process such as that described above.

The 2:1 reaction between $NaAlH_4$ and $BeCl_2$ in tetrahydrofuran produces soluble AlH_3 and an insoluble mixture of BeH_2 and NaCl. Attempted benzene

extraction of solvated $Be(AlH)_4$ from the reaction product of $LiAlH_4$ and $BeCl_2$ in tetrahydrofuran in 2:1 ratio yielded only solvated alane in 56 per cent yield as the soluble product. Therefore, no evidence of $Be(AlH_4)_2$ was found as the initial product of these reactions. In ether solvents, if $Be(AlH_4)_2$ is formed initially, disproportionation appears to be the predominant fate of this species. The observed redistribution of the products from the 2:1-$NaAlH_4$:$BeCl_2$ reaction in tetrahydrofuran could be explained as being due to catalysis by alkoxy-alane species arising from attack of AlH_3 on the solvent.

Again, the 1:1 reactions with $NaAlH_4$ in tetrahydrofuran are more complex than the 2:1 reactions. The insoluble product mixture was found to contain NaCl, BeH_2, and $BeCl_2 \cdot 2THF$ as the principal components. The soluble product does not contain $BeCl_2 \cdot 2THF$, and has an infrared absorption maximum at 1874 cm^{-1} and 1573 cm^{-1}. Analytical data suggests that the soluble species are AlH_3 and a compound of empirical formula HBeCl, possibly in combination as $ClBeAlH_4$; however, the Al:Be ratio is 1.73:1.0. Extended equilibration time might permit the insoluble product to react further to yield as final products, soluble $ClBeAlH_4$ and insoluble NaCl. The shift of the Al-H stretching frequency for this soluble 1:1 product to a value ca. 55 cm^{-1} above that for the absorption of the corresponding 2:1 product may reflect the effect of substituting chloride for aluminohydride in the proposed $Be(AlH_4)_2$. A corresponding shift is not observed for $Mg(AlH_4)_2$ and $ClMgAlH_4$ from tetrahydrofuran.[5]

A Study of the Thermal Decomposition of Complex Metal Hydrides

J. A. Dilts and E. C. Ashby

Abstract

The thermal decomposition of $LiAlH_4$, $NaAlH_4$, $KAlH_4$, $MAlH_4 \cdot L$ (L = tertiary amine, M = Li or Na), $ClMgAlH_4 \cdot 4THF$, $Mg(AlH_4)_2 \cdot 4THF$, Li_3AlH_6, Na_3AlH_6, and MgH_2 have been investigated using differential thermal analysis and thermogravimetric analysis. Evidence is presented that $MAlH_4$ compounds decompose through the corresponding M_3AlH_6. The amine complexes of $LiAlH_4$ have been demonstrated to have a higher thermal stability than the parent complex hydride. With $NaAlH_4$-amine complexes, desolvation precedes decomposition. However both $Mg(AlH_4)_2 \cdot 4THF$ and $ClMgAlH_4 \cdot 4THF$ undergo complex thermal decomposition involving loss of THF as well as THF cleavage.

Introduction

Few systematic studies on the manner of thermal decomposition of complex metal hydrides have been reported. Garner and Haycock[1] investigated time-decomposition curves for $LiAlH_4$ and concluded that decomposition occurred in three stages. The first of these was an initial surface reaction which was followed by loss of half of the hydridic hydrogen according to equation 1.

(1) W. E. Garner and E. W. Haycock, Proc. Roy. Soc., A211, 235 (1952).

$$LiAlH_4 \rightarrow LiAlH_2 + H_2 \qquad (1)$$

This in turn was followed by loss of the third hydrogen at a much slower rate (equation 2).

$$LiAlH_2 \rightarrow LiH + Al + 1/2\ H_2 \qquad (2)$$

Wiberg and coworkers have represented the thermal decomposition of $LiAlH_4$ in solution as occurring to give LiH directly (equation 3).

$$LiAlH_4 \rightarrow LiH + 3/2\ H_2 + Al \qquad (3)$$

This mode of decomposition has been suggested by these investigators for a number of complex metal hydrides.[2]

(2) E. Wiberg, Angew. Chem., 65, 16 (1953) and references therein.

Mikheeva and coworkers[3] examined the thermal decomposition of $LiAlH_4$ using combined differential thermal analysis (DTA) and effluent gas analysis (EGA). They found an endothermic effect at 154-161° accompanied by evolution of one mole of hydrogen. A second endothermic effect at 197-227° resulted in another half mole of hydrogen, with the final hydrogen evolution occurring at 580-586°.

(3) V. I. Mikheeva, M. S. Selivokhina, and O. N. Eryukova, Dokl. Akad. Nauk, SSSR, 109, 439 (1956).

Employing the technique of differential scanning calorimetry, Block and Gray[4] verified the three endothermic effects reported by Mikheeva in

(4) J. Block and A. P. Gray, Inorg. Chem., 4, 304 (1965).

addition to finding two exothermic effects. One of these was associated with decomposition resulting from a surface reaction as noted by Garner and Maycock earlier, and the second with the decomposition reaction shown in equation 1. They did not really insist that $LiAlH_2$ was a real compound, but the exothermic effect they observed was consistent with an EMF peak showing loss of one mole of hydrogen per mole of $LiAlH_4$. The endothermic effect that Mikheeva had associated with this decomposition was clearly demonstrated to be a reversible phase change by these workers.

The study of Maycock and coworkers[5] verified the results of Block and

(5) M. McCarty, Jr., J. N. Maycock, and V. R. Pai Verneker, J. Phys. Chem., 72, 4009 (1968).

Gray without adding anything to our understanding of the nature of $LiAlH_2$ which they also proposed as the product of the initial decomposition.

In a further study of the thermal decomposition by Mikheeva and Arkhipov,[6]

(6) V. I. Mikheeva and S. M. Arkhipov, Russ. J. Inorg. Chem., 12, 1066 (1967).

substantiation of the results of Block and Gray was made in addition to studying the effects of impurities on the decomposition reactions. These workers

suggested that the stoichiometry of equation 1 might represent the formation of Li_3AlH_6, a complex metal hydride reported by Ehrlich.[7] They confirmed this

(7) R. Ehrlich, A. R. Young, G. Rice, J. Dvorak, P. Shapiro, and H. F. Smith, J. Am. Chem. Soc., 88, 858 (1966).

conclusion by X-ray powder diffraction studies of partially decomposed $LiAlH_4$.

Ashby and Kobetz[8] reported that the controlled pyrolysis of $NaAlH_4$ lead

(8) E. C. Ashby and P. Kobetz, Inorg. Chem., 9, 325 (1966).

to the formation of Na_3AlH_6 which they had been able to prepare independently from sodium, aluminum, and hydrogen under high pressure.

$$3\ Na + Al + 3\ H_2 \rightarrow Na_3AlH_6 \qquad (4)$$

$$3\ NaAlH_4 \rightarrow Na_3AlH_6 + Al + 3\ H_2 \qquad (5)$$

We report here an initial account of a study covering several complex metal hydrides in an attempt to systematize the thermal decomposition of complex aluminum hydrides.

Experimental

Preparation of Compounds. - Lithium hydride was obtained from Alfa Inorganics as a 50% dispersion in mineral oil and used as obtained after washing several times with diethyl ether. Sodium hydride was also obtained commercially as a

mineral oil dispersion and similarly treated. KH was prepared from potassium metal and hydrogen in an autoclave. $LiAlH_4$ and $NaAlH_4$ were obtained commercially and recrystallized from ether and tetrahydrofuran- toluene respectively. $KAlH_4$ was prepared by the interaction of AlH_3 in diglyme with an excess of KH. The product was isolated by toluene precipitation. Magnesium aluminum hydride compounds were prepared as reported in the literature[9] as were amine adducts of $LiAlH_4$ and $NaAlH_4$.[10] Li_3AlH_6 and Na_3AlH_6 were prepared by literature methods.[11]

(9) E. C. Ashby, R. Schwartz, B. D. James, Inorg. Chem., 9, 325 (1970).

(10) J. A. Dilts and E. C. Ashby, Inorg. Chem., 9, 855 (1970).

(11) E. C. Ashby and B. D. James, Inorg. Chem., 8, 2468 (1969).

Simultaneous DTA-TGA measurements were performed on a Mettler Thermoanalyzer II. Samples were contained in either alumina or platinum crucibles using 60 mesh alumina in the reference crucible. Heating rates between 2 and 8°/minute were employed. Samples were loaded onto the thermoanalyzer under an atmosphere of argon and an argon atmosphere was maintained during the run. Sample weight was monitored on two sensitivities (usually 10 and 1 mg/inch) so that gross weight losses, e.g. solvent, as well as fine losses, hydrogen for example, could be observed.

Results

Our observations on the thermal decomposition of $LiAlH_4$ are in agreement with those of Mikheeva and Arkhipov. Figure 1 shows the clearly resolved

endothermic phase transition and exothermic effect, the latter being associated with a loss of weight. The second endothermic effect can be easily associated with the decomposition of Li_3AlH_6 as shown by the superimposition of the DTA curve for this compound. The last endothermic effect is due to the decomposition of LiH in both cases.

It is interesting to note that the decomposition of LiH formed from $LiAlH_4$ and Li_3AlH_6 appear to decompose at somewhat different temperatures. This clearly indicates the possibility of a solid state reaction between LiH and aluminum as has been suggested by Aronson and Salzano.[12] In the case of

(12) S. Aronson and F. J. Salzano, Inorg. Chem., 8, 1541 (1969).

Li_3AlH_6, less aluminum would be present for a given amount of LiH and one might expect that the decomposition of LiH would occur at a higher temperature than the relatively aluminum rich mixture obtained from the decomposition of $LiAlH_4$. This is observed.

In the case of $NaAlH_4$, the stepwise decomposition is not as well resolved as with $LiAlH_4$. Figure 2 shows the DTA-TGA plots for $NaAlH_4$. A strong endothermic effect (165-205°) proved to be reversible and is associated with a phase change. This endotherm is accompanied with a small weight loss if the hydride is not of a high degree of purity. Two subsequent endotherms are accompanied by weight losses corresponding to 75% of the hydrogen being given off. The TGA curve does not have a uniform slope and shows an inflection point consistent with the formation of Na_3AlH_6 according to equation 5. Comparison of the DTA curves for $NaAlH_4$ and Na_3AlH_6 suggests that the second of these endothermic effects

associated with the decomposition of Na_3AlH_6. The last endothermic effect (250-300°) results from the decomposition of NaH. Again the maximum of the NaH peak seems to show a dependence on the presence of aluminum. The effect is less pronounced than was observed in the decomposition of LiH.

The thermal decomposition of $KAlH_4$ is quite similar to that observed for $NaAlH_4$. The weight loss is not clearly resolved although an inflection point in the TGA curve is evident. Two endothermic effects correspond to a loss of 75 percent of the hydrogen and the third endotherm results from the final decomposition of KH as is shown by a superimposition of the DTA trace of KH (Figure 3).

Magnesium Hydride. - The thermal decomposition of MgH_2 prepared from the elements has been studied fairly extensively.[13,14,15] Extrapolation of the

(13) J. Bousguet, J. M. Blanchard, E. Bonnetet, P. Claudy, Bull. Soc. Chim. France, 21, 1841 (1969).

(14) J. Kennelly, J. W. Warraig and H. W. Myers, J. Phys. Chem., 64, 703 (1960).

(15) J. F. Stamper, Jr., C. E. Holley and J. F. Suttle, J. Am. Chem. Soc., 82, 3504 (1960).

decomposition temperatures obtained as a function of hydrogen pressure indicates a decomposition temperature of 300° for this form of MgH_2. MgH_2 may also be prepared by the reaction of a dialkyl magnesium compound with $LiAlH_4$.[16]

(16) G. D. Barbarus, C. Dilliard, A. E. Finholt, T. Warlik, K. E. Wilzbach, and H. I. Schlesinger, J. Am. Chem. Soc., 73, 4585 (1951).

Magnesium hydride prepared by this method, which used ether as the solvent, contains considerable (20%) ether. The DTA-TGA trace shown in Figure 4 indicates that most of this ether can be removed before the magnesium hydride begins to decompose at 330°. Magnesium hydride prepared by this method using THF as a solvent has a similar thermal stability to the ether containing hydride, but the shape of the DTA curve is considerably different. There is no evidence of THF cleavage and the difference in curve shapes may be a feature related to subtle differences in the physical state of the samples.

ClMgAlH$_4$ and Mg(AlH$_4$)$_2$. - The thermal decomposition of ClMgAlH$_4$·4 THF and Mg(AlH$_4$)$_2$·4 THF was also investigated. The thermal decomposition of these species is complicated by probable cleavage of Al-H bonds by THF. An endothermic effect in the decomposition of Mg(AlH$_4$)$_2$·4THF at 170° is accompanied by a weight loss greater than can be explained by loss of hydrogen alone (Figure 5).

The thermal decomposition of ClMgAlH$_4$·4THF and BrMgAlH$_4$·4THF are similar and only the ClMgAlH$_4$ case is shown (Figure 6). The endothermic effect at 110° is not suggestive of a desolvation process, but rather cleavage of aluminum-hydrogen bonds by THF. This is further supported by the high temperature weight loss. Between 200 and 400°, a weight loss corresponding to 13% of the original sample is observed while the maximum expected for decomposition loss of all hydridic hydrogen would be only 1.1%.

The decomposition of AlH$_3$ isolated from THF shows features similar to the decomposition curves for magnesium aluminum hydride (Figure 7), especially the low temperature exothermic effect followed by a high temperature weight loss (300-400°). Without EGA, it is not possible to characterize further the thermal

decomposition of these compounds.

$LiAlH_4$·ligand. - The TEDA (triethylenediamine) complex of $LiAlH_4$ shows two endothermic effects (Figure 8). The second of these is similar to the effect observed in the case of $LiAlH_4$ spectrum which was shown to be due to the decomposition of LiH in the presence of aluminum. The first effect which is associated with a major weight loss (196°, 76.2% weight loss, 77% calc for amine loss) corresponds to the decomposition

$$LiAlH_4 \cdot TEDA \xrightarrow{196°} LiH + TEDA + 3/2\ H_2 + Al \qquad (6)$$

The net effect of amine coordination is the stabilization of the complex metal hydride. At a point where decomposition becomes apparent, Li_3AlH_6 would already be decomposing (decomposition for Li_3AlH_6 starts at 182°) so this compound is not formed as an intermediate as it is in the case of the thermal decomposition of $LiAlH_4$ itself. It is also interesting to note that TEDA·AlH_3 has an appreciably higher decomposition temperature yet disproportionation as shown in equation 7 does not occur.

$$LiAlH_4 \cdot TEDA \rightarrow LiH + AlH_3 \cdot TEDA \qquad (7)$$

$(LiAlH_4)_2$·TMED has, in addition to the two endothermic decomposition effects, an endothermic peak associated with a reversible phase change (Figure 8). $LiAlH_4$·TMED shows two endothermic effects accompanied with the major (loss of ligand) weight loss. It was not possible to determine if one of these was due

to a phase change because their transition temperatures occurred so closely together. For clarity of presentation, TGA data was not plotted on Figure 5, but have been summarized with temperature data in Table 2.

<u>$NaAlH_4$ - Amine Complexes.</u> - The N,N',N'',N''' tetramethylethylenediamine complex of $NaAlH_4$ ($NaAlH_4 \cdot TMED$) decomposes thermally as expected for a simple solvate (Figure 9). The first endothermic effect is the result of a phase change and no weight loss was noted. The second endothermic effect is accompanied by loss of 59.6% of the weight of the sample (Calcd. for $NaAlH_4 \cdot TMED$, 68.3%). The remaining three endothermic effects are consistent with the decomposition of $NaAlH_4$ which is shown superimposed on the $NaAlH_4 \cdot TMED$ trace. Differences in the location of the peak are not surprising in light of the different heating rates used (Table 2).

The interpretation of the data for decomposition of $NaAlH_4 \cdot TEDA$ is not so clear cut (Figure 10). While the last endothermic effect corresponds to the decomposition of NaH, the exact nature of the decomposition leading to this product is not clear. For example the weight loss for the first exothermic effect corresponds to loss of all the TEDA. The hydrogen loss however cannot be resolved in the massive weight loss of the amine. The DTA peak corresponding to this weight loss is in the same region as the decomposition of $NaAlH_4$ and may be a composite of the three processes,

$$NaAlH_4 \cdot TEDA \rightarrow NaAlH_4 + TEDA \qquad (8)$$

$$3\ NaAlH_4 \rightarrow Na_3AlH_6 + 2\ Al + 3\ H_2 \qquad (9)$$

$$Na_3AlH_6 \rightarrow Al + 3\ NaH + 3/2\ H_2 \qquad (10)$$

or

$$3\ NaAlH_4 \cdot TEDA \rightarrow Na_3AlH_6 + 3\ TEDA + 3\ H_2 \qquad (11)$$

followed by equation 10

or

$$NaAlH_4 \cdot TEDA \rightarrow NaH + Al + 3/2\ H_2 + TEDA \qquad (12)$$

In light of the behavior of $NaAlH_4 \cdot TMED$, the first sequence of reactions seems most plausible. Further there appears to be a good correlation between the shoulder on the first endothermic effect and the endothermic effect of the $NaAlH_4 \cdot TMED$ decomposition which is attributed to the decomposition of Na_3AlH_6. This is only indirect evidence however.

Discussion

The first generalization concerning the thermal decomposition of complex metal hydrides is that the same order of stability (with respect to the nature of M) of $MAlH_4$ compounds as compared to MBH_4 compounds has been found.[17]

(17) D. S. Stasinevich and G. A. Egorenko, Russ. J. Inorg. Chem., 13, 341 (1968).

The increase in stability follows the increase in cation size (Li < Na < K) and the simple interpretation of this order is based on increasing stabilizing power

of the larger cation. Although it is difficult to put this argument on a sound quantitative basis, the suggestion that the degree of distortion of the BH_4^- tetrahedron strongly effects chemical behavior of BH_4 compounds, has been made.[18]

(18) H. I. Schlesinger and H. C. Brown, J. Am. Chem. Soc., 62, 3429 (1940).

While our results with $LiAlH_4$ substantiate the general finds of Block and Gray,[4] as well as McCarty, Maycock, and Verneker,[5] there are several points of difference in interpretation of the DTA-TGA data.

The work reported here was performed on a $LiAlH_4$ sample that had been twice recrystallized (once from ether and once from ether-benzene); we failed to observe the first exothermic transtion that Block and Gray attributed to a surface reaction and McCarty et al. attributed to a melting of $LiAlH_4$. The presence of ether may account for this exotherm and/or the darkening of $LiAlH_4$ at this point. Our samples were essentially ether free and no darkening of the sample was noted through the first endothermic effect. In further contrast to McCarty et al. suggestion, even slow scan rates (2°/minute) still showed a distinct endothermic effect.

While nothing definite was concluded about the nature of the impurity giving rise to the exothermic effect observed by these two groups, the work of Dymova et. al.[19] on the thermal decomposition of $LiAlH_4 \cdot nAlH_3$ species is quite

(19) T. N. Dymova, M. S. Roshchina, E. S. Grazhulene, and V. A. Kuznetzov, Dokl. Akad. Nauk SSSR, 184, 1338 (1969).

similar to the behavior observed in the impure $LiAlH_4$ samples. The compound claimed to be Li_2AlH_7 decomposed with a strong exothermic effect from 160-220°.

The exothermic effect following the endothermic phase transition (only exotherm of Figure 1) has widely been interpreted as indicating the formation of $LiAlH_2$. Recent work[5] has shown that this compound is most probably Li_3AlH_6. Comparison of the thermograms of an authentic sample of Li_3AlH_6 support this conclusion. (Figure 1)

The thermal decomposition of $LiAlH_4$ is then summarized by the following equations.

$$3\ LiAlH_4 \rightarrow Li_3AlH_6 + 3\ H_2 + 2\ Al \qquad (13)$$

$$Li_3AlH_6 \rightarrow 3\ LiH + 3/2\ H_2 + Al \qquad (14)$$

$$LiH + Al \rightarrow \text{"LiAl"} + 1/2\ H_2 \qquad (15)$$

The last reaction is of interest in that pure LiH melts with little decomposition at 680° while LiH in the presence of Al metal has been shown to decompose at much lower temperatures, presumably involving a solid state reaction between LiH and Al.[12] A thorough study of this reaction has not been made, but it would appear that there is some dependence of the temperature of decomposition on the ratio of LiH to Al metal.

Results from the DTA-TGA study of $NaAlH_4$ and $KAlH_4$ suggest that these complex metal hydrides decompose by a mechanism similar to that found for $LiAlH_4$.

Figure 2 illustrates a typical result for the thermal decomposition of $NaAlH_4$. Following a strong endothermic effect which is reversible and associated with a phase change, two endothermic effects (212-250° and 250-300°) occur concurrently with loss of 75% of the hydridic hydrogen. Although a clear break in the TGA curve is not evident, there is an inflection point suggesting that the loss of hydrogen is occurring in two steps (Equations 16, 17).

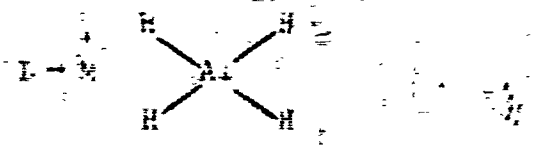
$$3\ NaAlH_4 \rightarrow Na_3AlH_6 + 3\ H_2 + 2\ Al \qquad (16)$$

$$Na_3AlH_6 \rightarrow 3\ NaH + Al + 3/2\ H_2 \qquad (17)$$

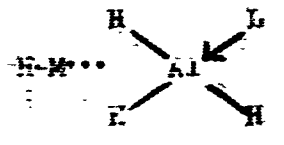
The high temperature endotherm (300-402°) is most reasonably assigned to the decomposition of NaH. The conclusion that $NaAlH_4$ decomposes through Na_3AlH_6 is supported by the thermal decomposition of an authentic sample of the latter which undergoes decomposition in the same region as the third endothermic effect found with $NaAlH_4$.

The DTA-TGA trace for $KAlH_4$ shows three endothermic effects which are accompanied by weight loss. Again the formation of K_3AlH_6 is not clearly resolved in the TGA curve, but is strongly suggested by an inflection in this curve.

Complexes of the type $MAlH_4 \cdot L$ (M = Li or Na and L = tertiary amine) have been assigned two probable structures on the basis of infrared data (I and II below).



I



II

The thermal decomposition of a species such as I might be expected to be similar to that of the parent complex hydride, especially if coordination were weak. Decomposition of II might be expected to be more complicated in light of the amine alane character this compound would be expected to show. A prediction regarding the relative thermal stabilities of these two alternatives is also possible. The net effect of structure I would be a reduction in the distortion of the AlH_4 tetrahedron through covalent interaction with the alkali metal as well as effectively increasing the size of the cation. In light of the increasing thermal stability of the $MAlH_4$ series, it is anticipated that such a structure would result in an enhanced thermal stability. Increasing the AlH_3 character as is the case in structure II might be anticipated to reduce the thermal stability.

The $NaAlH_4 \cdot TMEN$ thermal decomposition involves the initial loss of amine (80-154°) followed by decomposition of the remaining $NaAlH_4$ (Figure 9). Interpretation of the thermal decomposition of $NaAlH_4 \cdot TMEA$ is more complex. The endothermic effect occurring from 191-295° reflects a weight loss corresponding to loss of all the amine (Table 2). A shoulder on this endotherm suggests that concurrent with the loss of amine, $NaAlH_4$ may be decomposing to give Na_3AlH_6 whose decomposition is reflected by the shoulder at 260°. NaH is produced as a result of this decomposition as evidenced by an endothermic effect at 340-425°.

No clear desolvation steps were found with the amine complexes of $LiAlH_4$. Enhanced thermal stability of the amine complexes over $LiAlH_4$ itself (and Li_3AlH_6) result in the ambiguous nature of the DTA-TGA curves. It is not possible to resolve the question of the possible formation of Li_3AlH_6 in the course of the decomposition. In the cases investigated, LiH is the end product as evidenced by its characteristic endothermic decomposition. It is not possible to say if this LiH is produced directly from the decomposition or from an Li_3AlH_6 intermediate.

$$LiAlH_4 \cdot L \rightarrow LiH + Al + 3/2\ H_2 + L \qquad (18)$$

or

$$3\ LiAlH_4 \cdot L \rightarrow Li_3AlH_6 + 2\ Al + 6\ H_2 + 3\ L \qquad (19)$$

The thermal decomposition of species involving the AlH_4 group and Mg is not straightforward. Several workers have observed that borohydride analogues as THF solvates cannot be desolvated by heating under vacuum without loss of boron from the compound as volatile ether-borane.[10,20] The same

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(20) J. Plešek and S. Heřmánek, Collection Czech. chem. Commun., 31, 3845 (1966).

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problem of THF cleavage appears to be occurring in the case of $ClMgAlH_4 \cdot 4THF$ and $Mg(AlH_4)_2 \cdot 4THF$. The absence of any effects in the DTA trace which could be assigned to MgH, suggests that this is not produced in the initial thermal decomposition (Figures -, -, -). The thermal decomposition of $(AlH_3)_4THF$

(Figure 7) shows a number of features which are suggestive that some alkoxy aluminum species may be present in the decomposition product of these complex magnesium hydrides.

Table 1

Thermal Decomposition of Alkali Metal Complex Hydrides

Compound	Thermoicity	Range of Transition	% weight loss
$NaAlH_4$ [a]	Endo	165-205	(phase change)
	Endo	212-250	3.37 } 5.43
	Endo	250-300	2.06 }
	Endo	300-402	1.63
$LiAlH_4$ [a]	Endo	150-	(phase change)
	Exo	-175	4.25
	Endo	180-224	1.97
	Endo	362-425	1.76
$KAlH_4$ [a]	Endo	235-280	} 3.63
	Endo	280-320	
	Endo	320-380	0.77
Li_3AlH_6 [a]	Endo	182-227	
	Endo	370-455	
Na_3AlH_6 [b]	Endo	223-305	ratio of wt. loss
	Endo	305-405	0.97:1

a Heating rate = 2°/min

b Heating rate = 4°/min

Table 2

Thermal Decomposition of Complex Metal Hydride Amine Adducts

Compound	Thermoicity	Range of Transition	% Weight Loss
$LiAlH_4 \cdot TEDA$[a]	Endo	196-238	76.2
	Endo	340-425	0.35
$LiAlH_4 \cdot TMED$[a]	Endo	175-180	
	Endo	182-205	73.1
	Endo	360-430	0.36
$(LiAlH_4)_2 TMED$[c]	Endo	100-132	Phase Change
	Endo	167-207	56.1
	Endo	395-420	0.77
$AlH_3 \cdot TEDA$[a]	Endo	200-238	----
$NaAlH_4 \cdot TEDA$[a]	Endo	195-290	59.6
	Endo	sh. max. 260	----
	Endo	290-370	0.56
$NaAlH_4 \cdot TMED$[b]	Endo	35-50	Phase Change
	Endo	80-154	60.42
	Endo	163-200	Phase Change
	Endo	235-250	1.26
	Endo	250-290	
	Endo	290-365	0.42

a Heating rate = 2°/min

b Heating rate = 4°/min

c Heating rate = 6°/min

Table 3

Thermal Decomposition of Magnesium Hydride Species

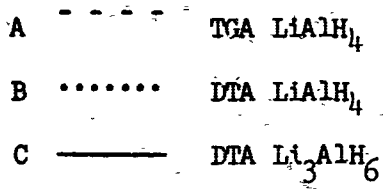
Compound	Thermoicity	Range of Transition	% Weight Loss
$MgH_2(THF)$[b]	Endo	345-425	----
$MgH_2(Ether)$[a]	Endo	320-360	----
$(AlH_4)_4THF$[a]	Exo	35-90	34.4
	Endo	120-172	5.4
	Endo	172-192	
	Endo	205-230	
	Exo	360-495	16.4
	Exo	495-510	
$ClMgAlH_4 \cdot 4THF$[a]	Endo	50-87	19.6
	Endo	87-115	16.3
	Exo	115-160	11.9
	Endo	160-297	5.9
	Endo	297-322	14.1
	Endo	322-345	
$Mg(AlH_4)_2 \cdot THF$[c]	Endo	92-170	38.4
	Exo	170-188	26.1
	Endo	330-377	4.9
	Endo	421-440	

a Heating rate = 2°/min

b Heating rate = 4°/min

c Heating rate = 6°/min

Figure 1



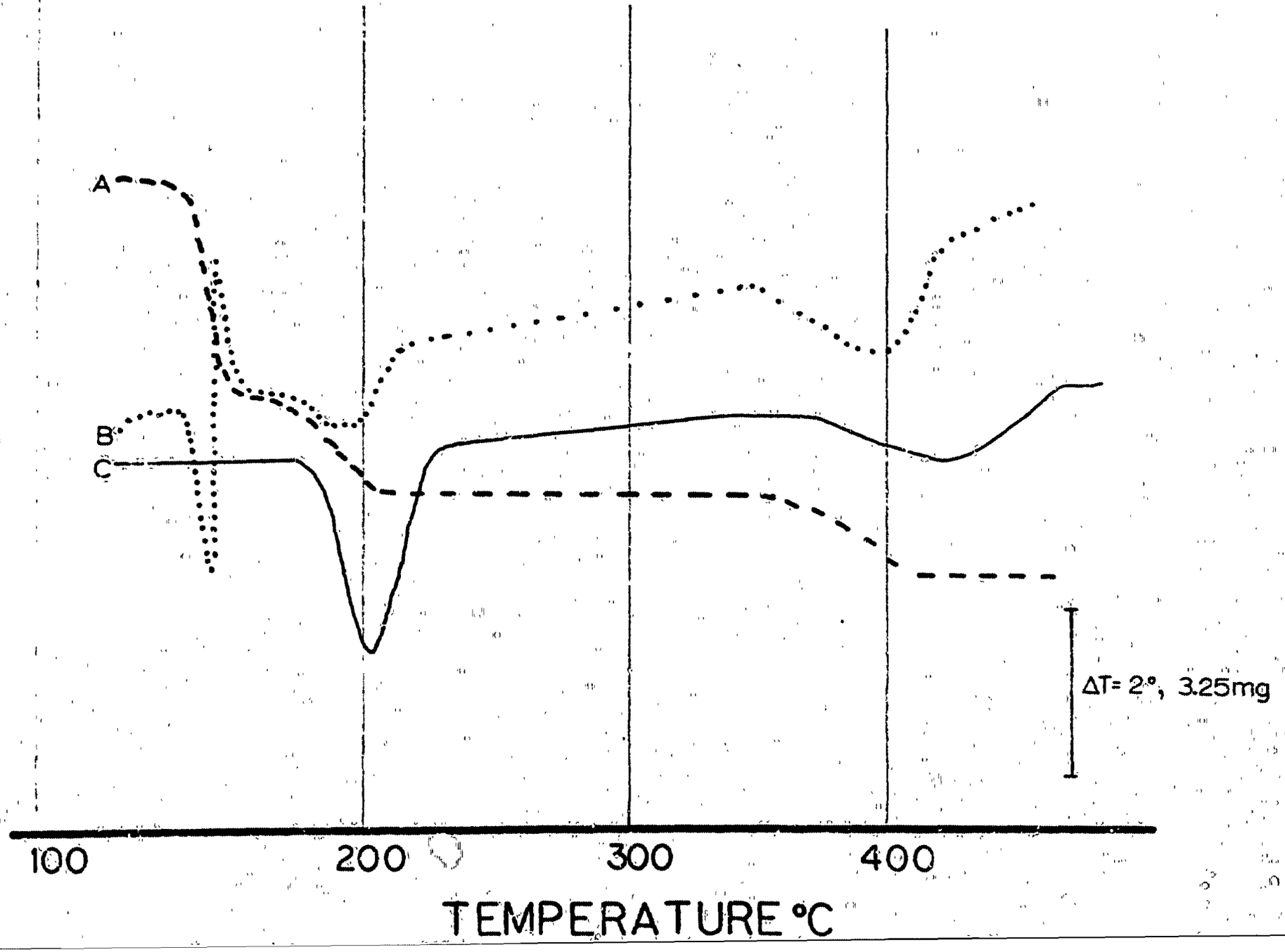
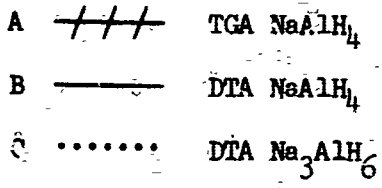

A
B
C
ΔT= 2°, 3.25mg
100
200
300
400
TEMPERATURE °C

Figure 2



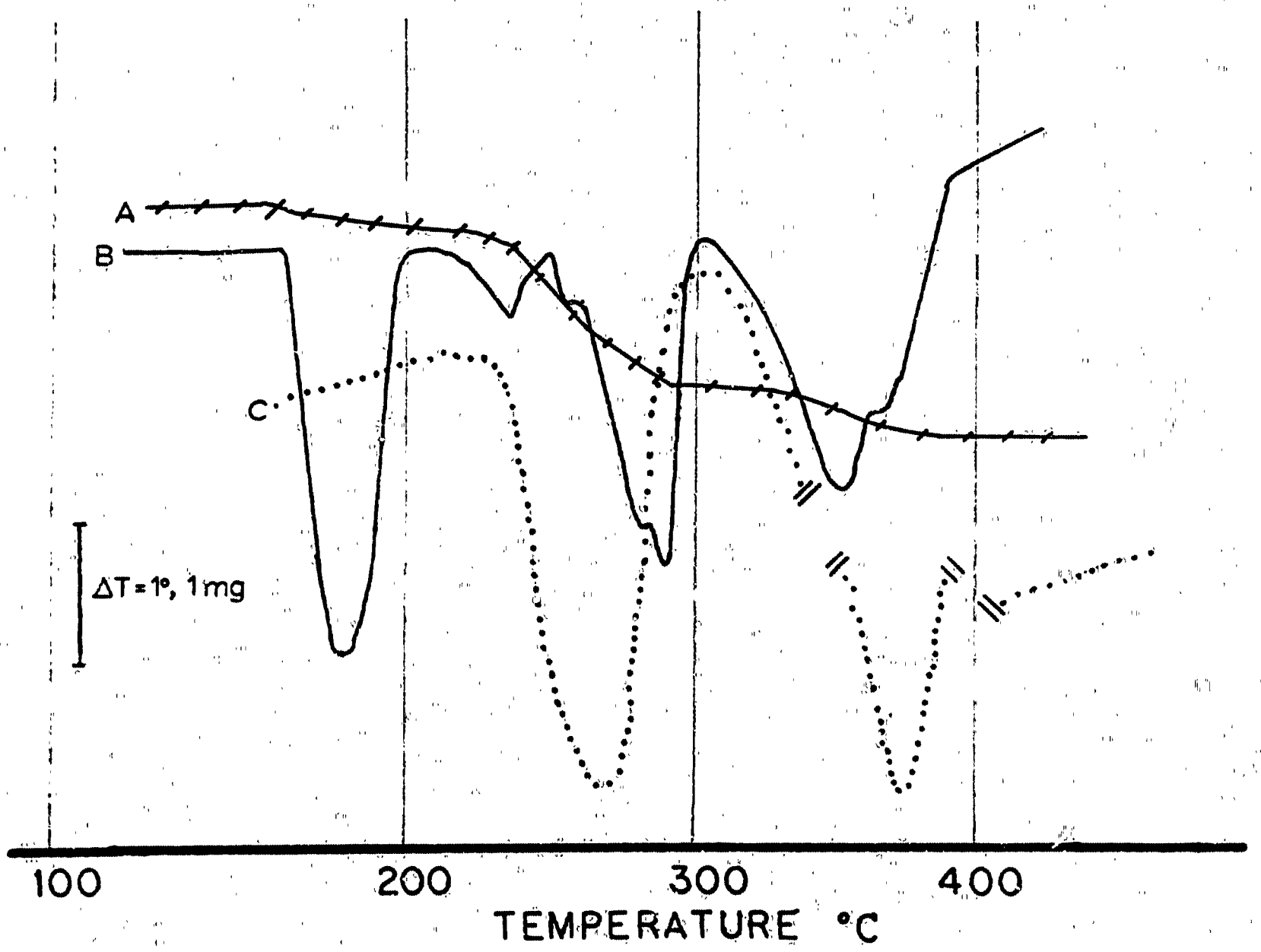

A
B
C
ΔT = 1°, 1mg
100
200
300
400
TEMPERATURE °C

Figure 3

A ——— TGA $KAlH_4$

B ····· DTA $KAlH_4$

C ——— DTA KH

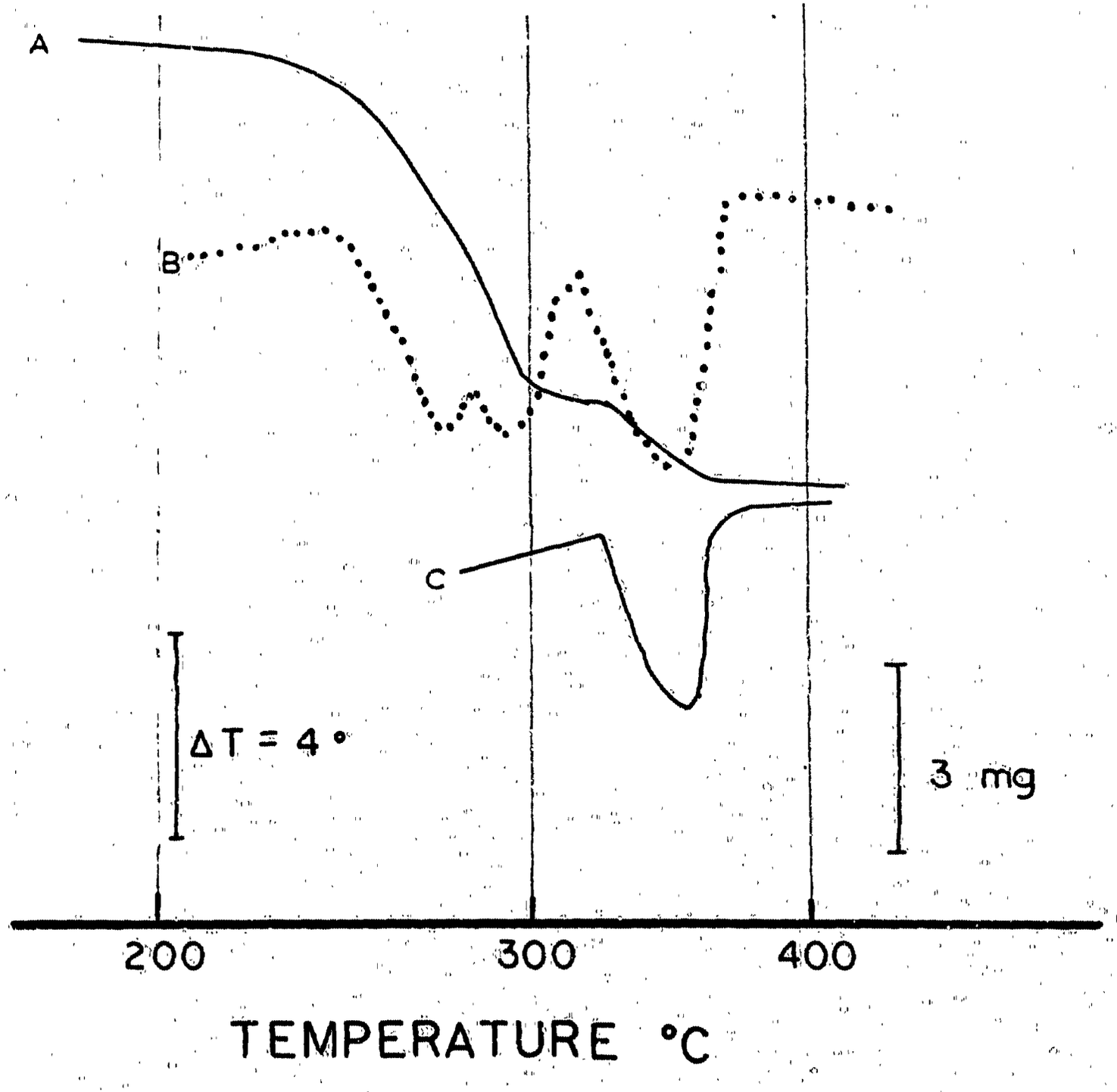

A
B
C
ΔT = 4°
3 mg
200
300
400
TEMPERATURE °C

Figure 4

A ····· DTA MgH_2 from THF

B - - - - TGA MgH_2 from $(C_2H_5)_2O$

C ~~/ / /~~ 10XTGA MgH_2 from $(C_2H_5)_2O$

D ——— DTA MgH_2 from $(C_2H_5)_2O$

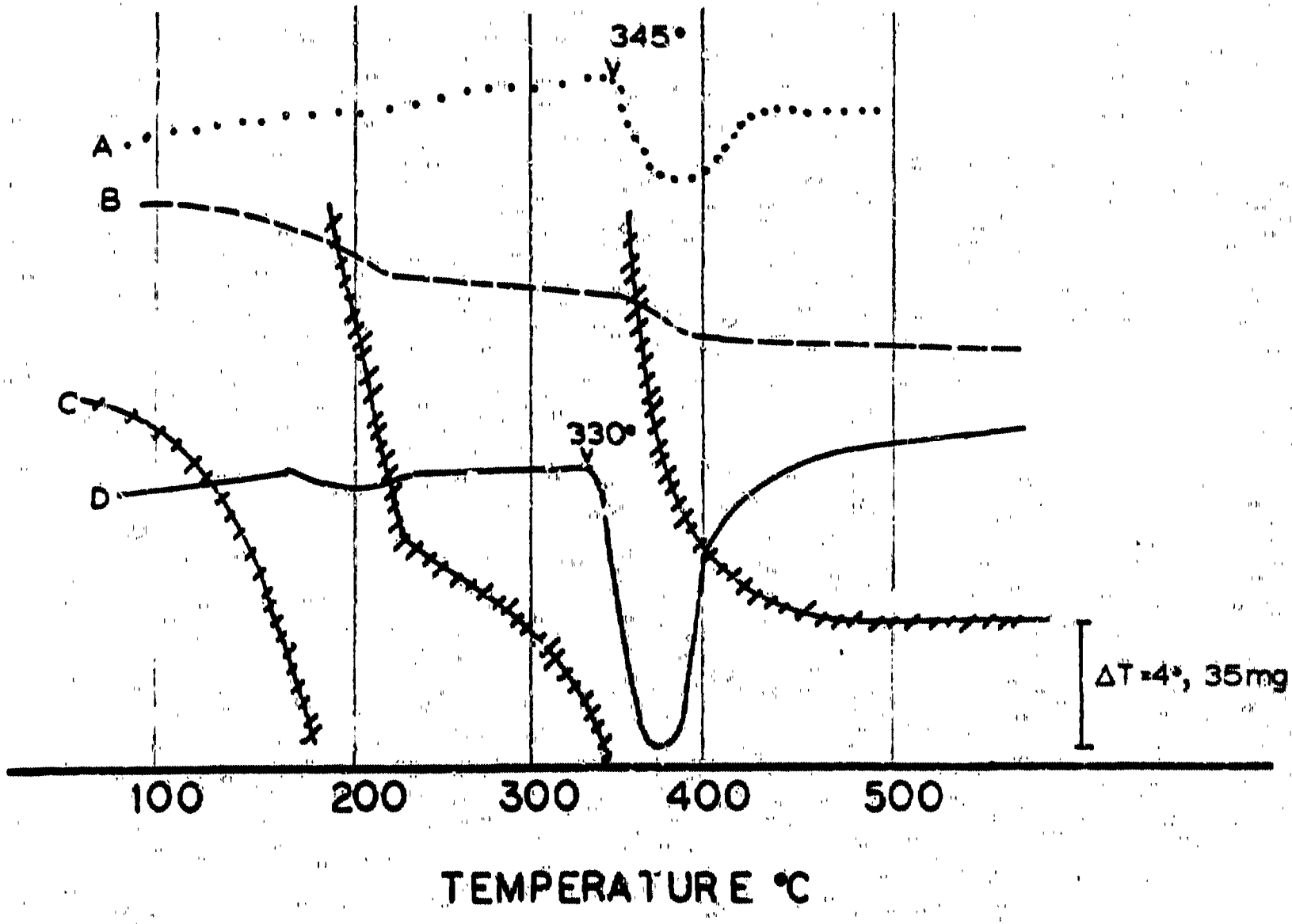

345°
A
B
C
330°
D
ΔT=4°, 35mg
100
200
300
400
500
TEMPERATURE °C

Figure 5

A ····· TGA of $Mg(AlH_4)_2 4THF$

B ——— DTA of $Mg(AlH_4)_2 4THF$

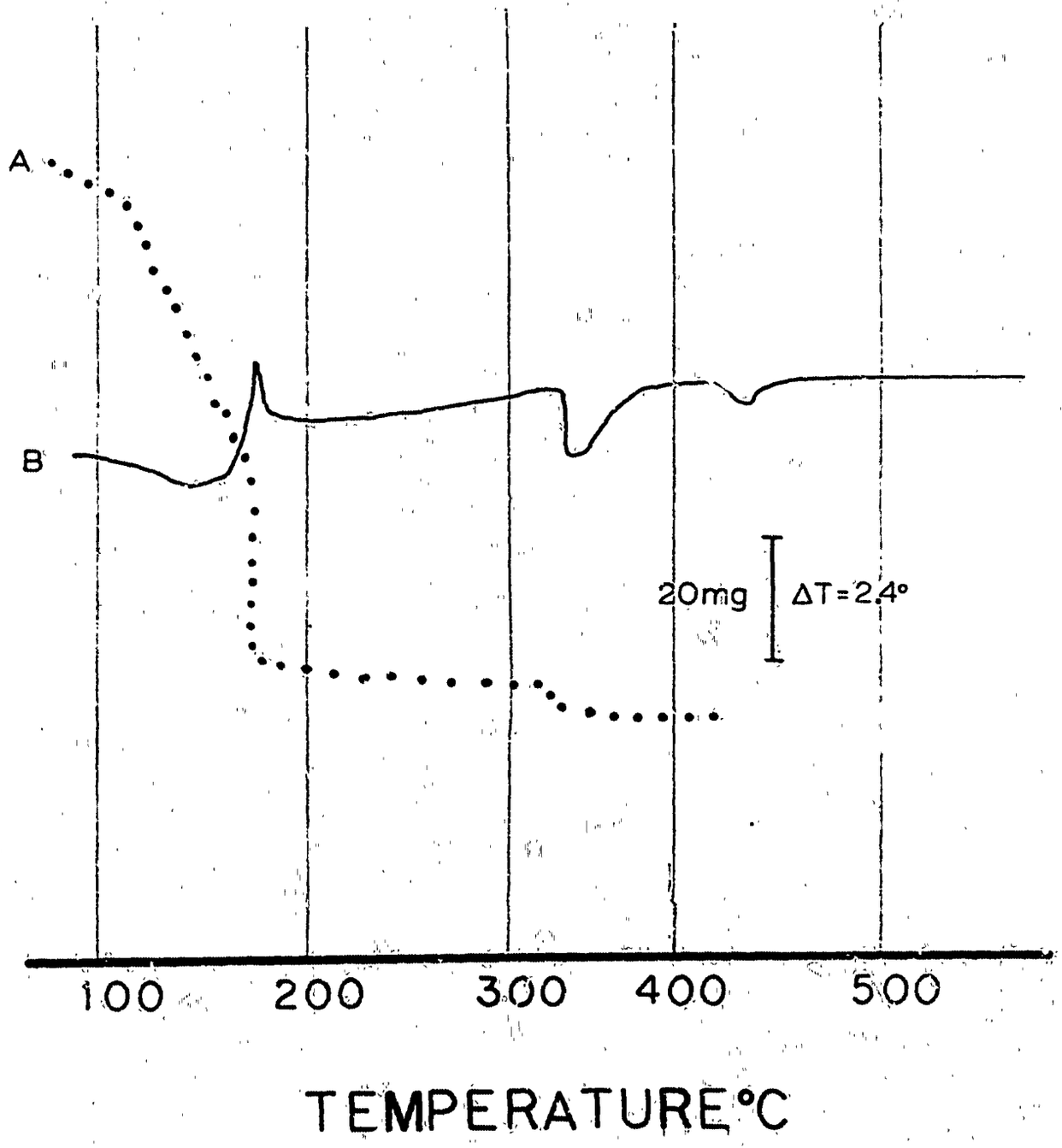

A
B
20mg
ΔT=2.4°
100
200
300
400
500
TEMPERATURE °C

Figure 6

A ——— TGA of $ClMgAlH_4 4THF$

B ····· DTA of $ClMgAlH_4 4THF$

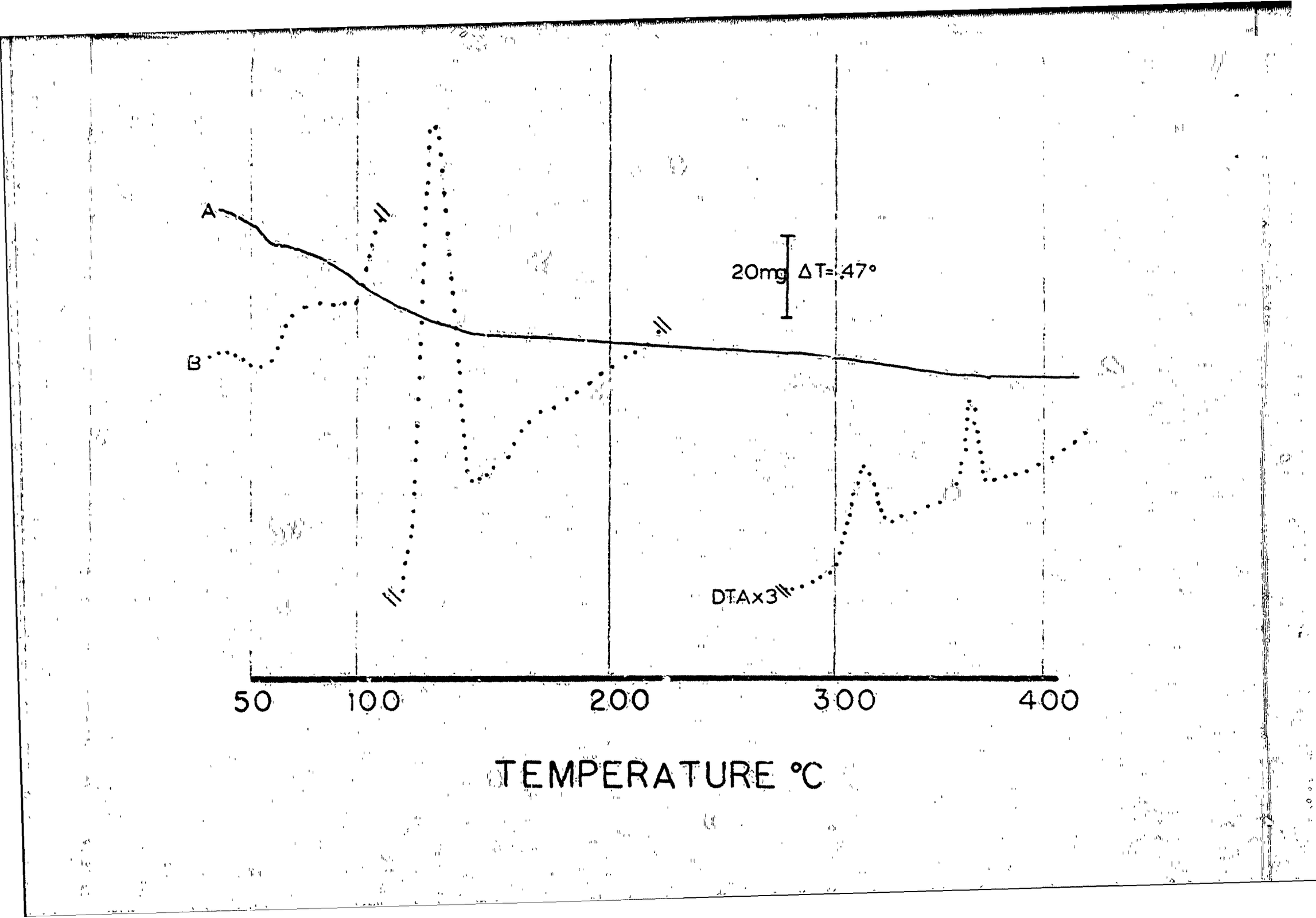

A
B
20mg
ΔT=.47°
DTAx3
50
100
200
300
400
TEMPERATURE °C

Figure 7

A ——— TGA of AlH_3 from THF

B ····· DTA of AlH_3 from THF

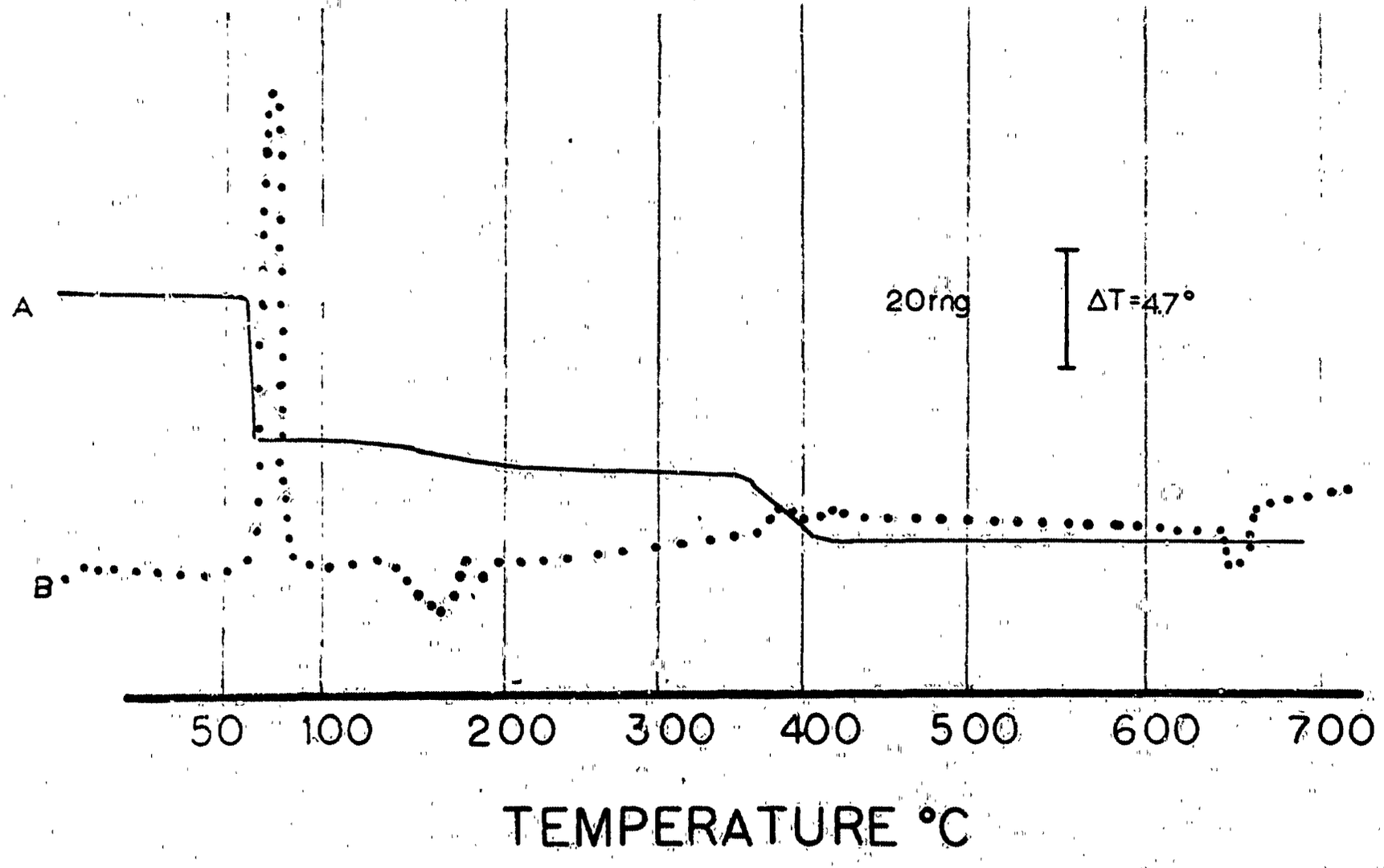

A
B
20mg
ΔT=47°
50
100
200
300
400
500
600
700
TEMPERATURE °C

Figure 8

A ····· $LiAlH_4 \cdot TMED$, DTA

B -·-·-·- TGA $LiAlH_4 \cdot TEDA$

C ——— DTA $(LiAlH_4)_2 \cdot TMED$

D -·-·-·- DTA $LiAlH_4 \cdot TEDA$

E ····· $AlH_3 \cdot TEDA$, DTA

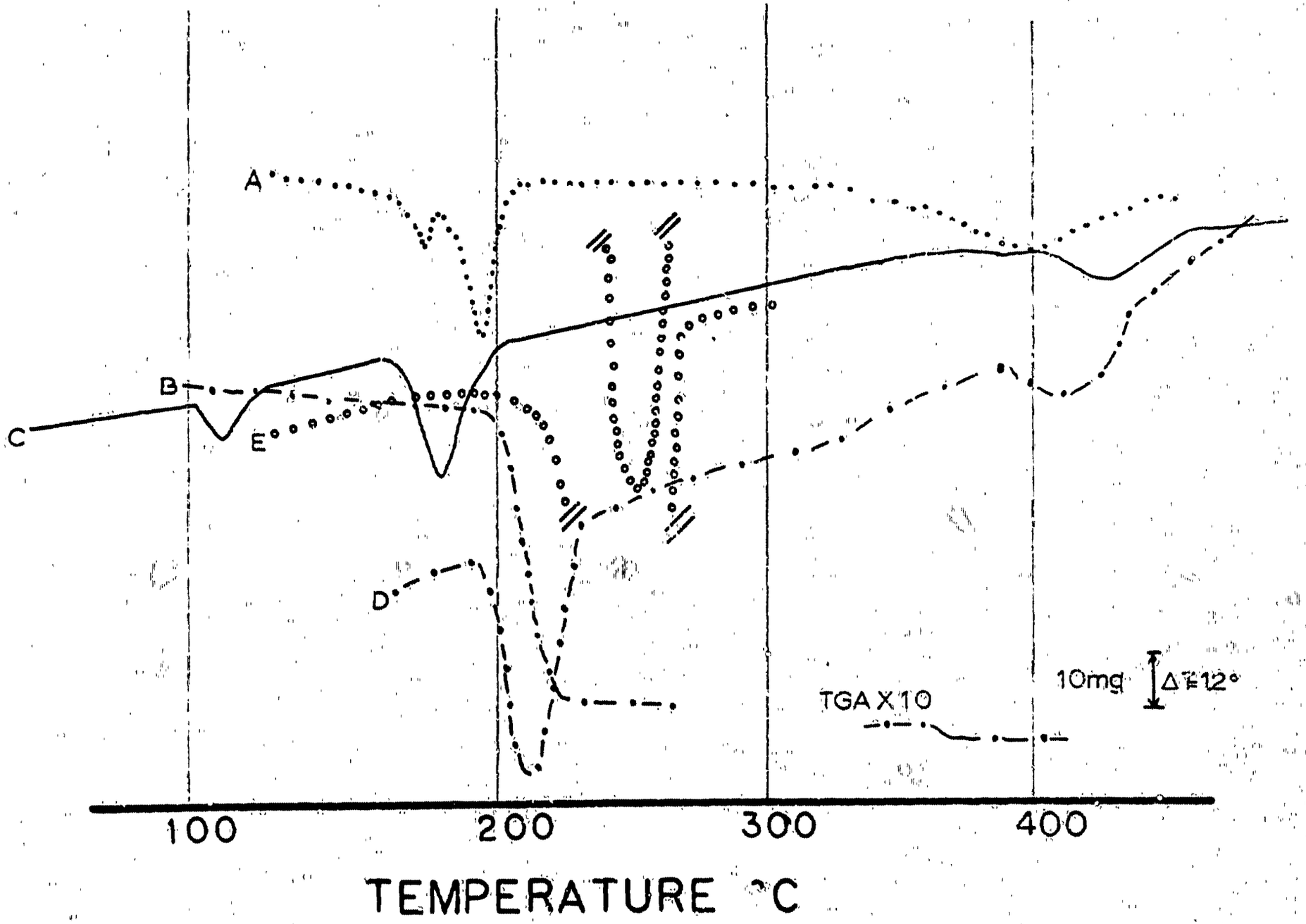

A
B
C
E
D
TGA X 10
10mg
ΔT=12°
100
200
300
400
TEMPERATURE °C

Figure 9

A ——— TGA $NaAlH_4$·TMED

B ——— DTA $NaAlH_4$·TMED

C ····· DTA $NaAlH_4$

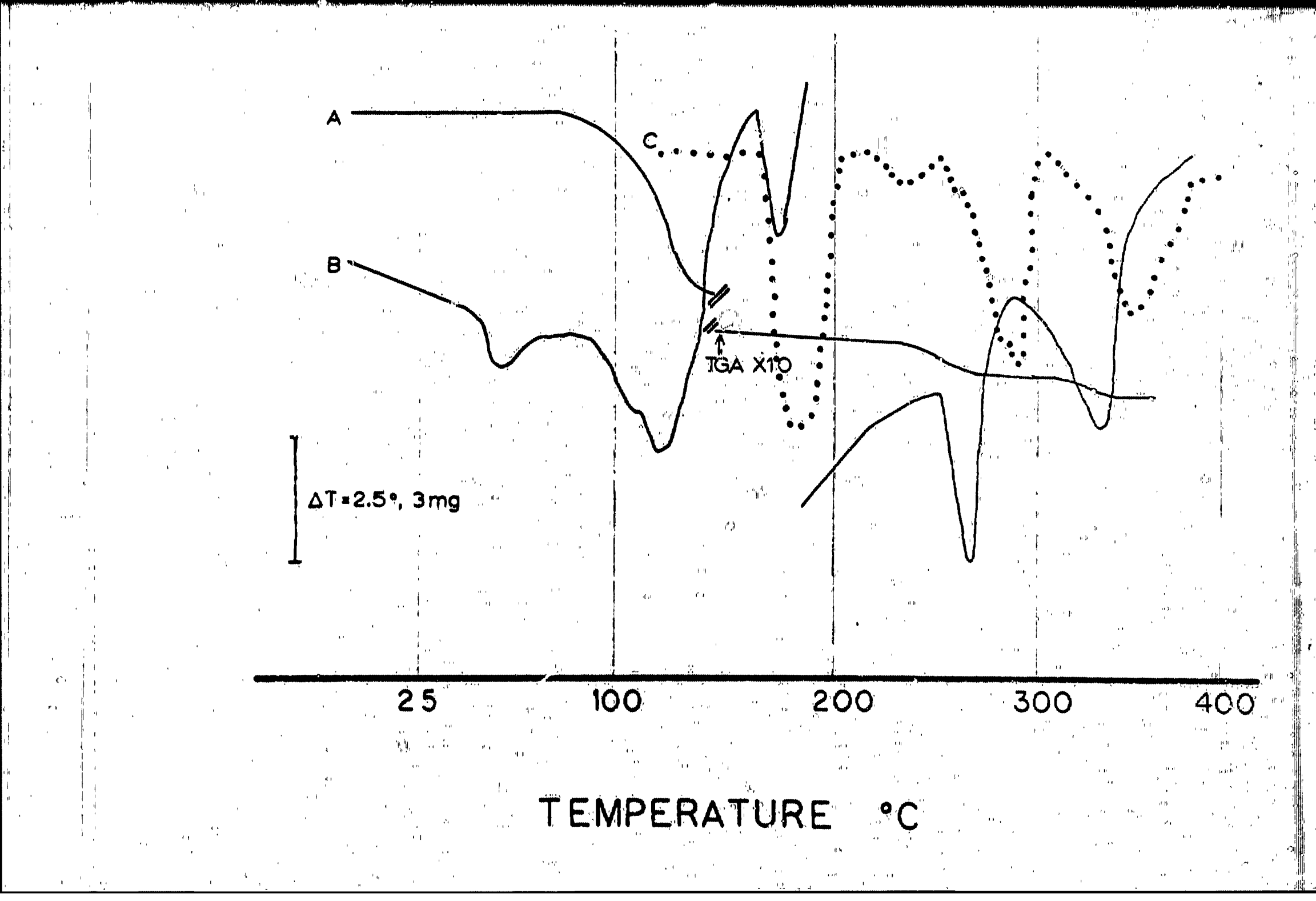
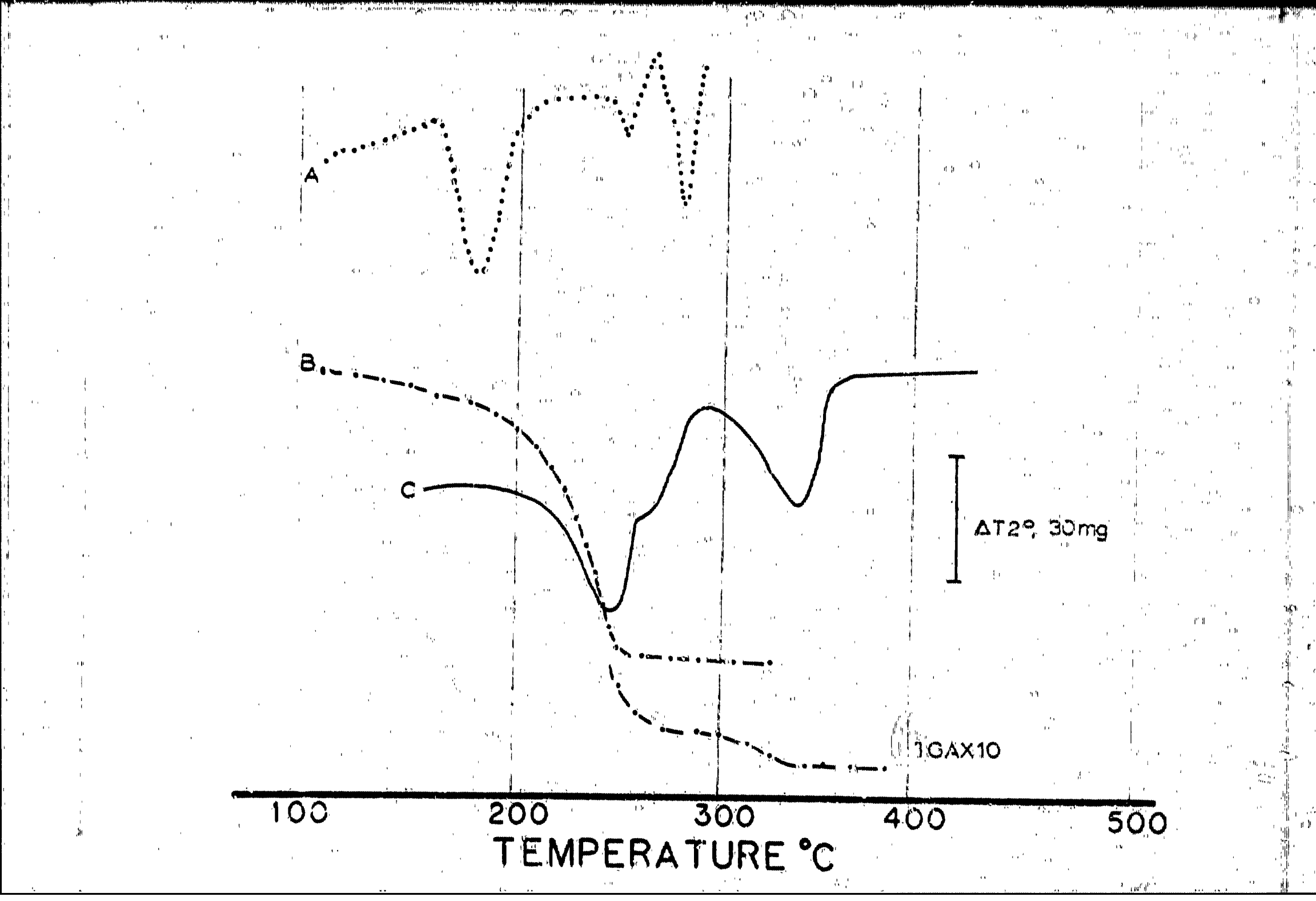

A
B
C
TGA X10
ΔT=2.5°, 3mg
25
100
200
300
400
TEMPERATURE °C

Figure 10

A ····· DTA for $NaAlH_4$ (not showing NaH decomposition)

B -·-·-·- TGA for $NaAlH_4$·TEDA

C ——— DTA for $NaAlH_4$·TEDA


A
B
C
ΔT2°, 30mg
TGAX10
100
200
300
400
500
TEMPERATURE °C

Synthesis of Alkyl Magnesium Hydride

E. C. Ashby and H. T. Wall

Abstract

The synthesis of alkyl magnesium hydrides by several different pathways is now under investigation. These include (1) pyrolysis and hydrogenation of dialkylmagnesium compounds, (2) reduction of Grignard reagents and (3) redistribution of dialkylmagnesium compounds with magnesium hydrides.

$$(RCH_2CH_2)_2Mg \xrightarrow{H_2} RCH_2CH_3 + RCH_2CH_2MgH \quad (1)$$

$$\searrow^{\Delta} \quad RCH{=}CH_2 + RCH_2CH_2MgH \quad (2)$$

$$RMgX + NaH \rightarrow NaX + RMgH \quad (3)$$

$$R_2Mg + MgH_2 \rightarrow 2(RMgH) \quad (4)$$

Introduction

G. E. Coates, et al.,[1] have reported that diethylmagnesium and sodium triethylhydridoborate redistribute to give diethylmagnesium and magnesium hydride at 0° in diethyl ether. When the reaction was carried out at -78°, no

(1) G. E. Coates and J. A. Heslop, J. Chem. Soc. (A), 514 (1968).

magnesium hydride precipitated. At -78° a sample was taken from the reaction flask and hydrolyzed. The analysis gave an ethane:hydride ratio of 1:1. If the original reactants had been present the ethane:hydride ratio would have been 2:1 for an equimolar mixture of diethylmagnesium and sodium triethylhydridoborate. The following reaction was proposed:

$$NaEt_3BH + Et_2Mg \rightleftharpoons EtMgH + NaEt_4B \qquad (5)$$

Coates reported that ethylmagnesium hydride is stable at -78° but starts to disproportionate at -20° causing magnesium hydride to precipitate.

$$2(EtMgH) \rightleftharpoons Et_2Mg + MgH_2 \qquad (6)$$

Since disproportionation of ethylmagnesium hydride would be expected to be more facile in diethyl ether, most of the proposed syntheses for alkyl magnesium hydrides were carried out in hydrocarbon solvents. Alkylmagnesium compounds other than ethyl are being investigated in the hope that they will prove more stable at room temperature.

Experimental

Apparatus. - A Mettler DTA-TGA was used to study the thermal decompositions of dialkylmagnesium compounds. Chemical reactions and manipulations were accomplished by use of dry nitrogen bench-top techniques or in a nitrogen filled glove box. Infrared spectra were obtained on a Perkin-Elmer 621 Spectrophotometer. Cesium Iodide liquid and mull cells were used. A 60 cycle Varian A-60 was used for nmr

spectra. Gas analysis was carried out on a high vacuum line.[2]

(2) D. F. Shriver, The Manipulation of Air-Sensitive Compounds, McGraw-Hill, New York, New York, (1969).

Analytical. - Halogen analysis was performed by the Volhard method. Magnesium analysis was carried out by titration with EDTA. Aluminum analysis was carried out by excess EDTA addition and back titration with zinc acetate solution.

Reagents. - Benzyl chloride was dried over calcium chloride then distilled under vacuum. Alkyl halides were dried over calcium chloride then distilled. Diethyl ether was distilled over lithium aluminum hydride. Sodium hydride in mineral oil was obtained from Ventron Metal Hydrides, Inc. Benzene was distilled over sodium aluminum hydride. s-Butyllithium in cyclohexane was obtained from Lithium Corporation of America.

Preparation of Di-s-Butylmagnesium.[3] - A solution of s-butylmagnesium (1 molar)

(3) Conrad Kamienski and Jerome F. Eastham, J. Org. Chem., 34, 1116 (1969).

in diethyl ether was prepared from s-butylchloride and magnesium metal. The analysis of the resulting solution indicated a butane:magnesium:chlorine ratio of 1.01:1.00:1.14. The Grignard reagent was refluxed and benzyl chloride added in 250 mmolar amounts until 1 mole had been added. Magnesium chloride precipitated. The precipitate was isolated by filtration and washed with benzene. The last trace of ether was removed by codistillation with benzene. An analysis of the magnesium chloride indicated a magnesium:chlorine ratio of 1.00:1.90. A molar

quantity of n-butyllithium equal to 7½ of the chloride concentration was added and stirred at 40°C over a period of 2 hours. Lithium chloride precipitated leaving di-n-butylmagnesium in a mixed solvent of benzene and cyclohexane. The lithium chloride was filtered and the solvent removed *in vacuo*. The di-n-butylmagnesium was redissolved in benzene. An analysis of the solution indicated a butane:magnesium ratio of 1.9:1.00. An nmr spectra of the solution showed the following absorptions: 9.09 τ (multiplet), 8.77 τ (triplet), 8.43 τ (doublet), 8.0 τ (multiplet) and an absorption centered at 6.57 τ due to a trace of ether.

Sodium Hydride and n-Butylmagnesium Chloride. - Sodium hydride (25 mmole) was stirred with n-butylmagnesium chloride (25 mmole) in 100 ml of triethylamine over a period of 3 days. The insoluble material was filtered and dried *in vacuo* at 25°. Analysis of the residue indicated a sodium:hydrogen ratio of 1.00:1.00; magnesium and chlorine were absent. The analysis of the filtrate indicated a butane:magnesium:chlorine ratio of 1.00:0.98:1.03; hydrogen was absent.

Lithium Hydride and n-Butylmagnesium Chloride·Triethylaminate. - A solution of n-butylmagnesium chloride·triethylaminate[4] (0.3 molar) was prepared in benzene.[3]

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(4) S. C. Ashby and R. Reed, J. Org. Chem., 31, 971 (1966).

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[3] Analysis indicated a n-butane:magnesium:chlorine ratio of 1.00:1.00:1.08. Lithium hydride was prepared via hydrogenation of t-butyllithium at 3000 psig and 25°. The analysis indicated a lithium:hydrogen ratio of 1.00:1.00. Lithium hydride (20 mmoles) was stirred with n-butylmagnesium chloride·triethylaminate

(40 mmole) over a period of 4 days. The residue was filtered and analysis indicated a lithium:hydride ratio of 1.00:1.00 and chloride was absent. The filtrate analysis indicated a magnesium:chlorine ratio of 1.03:1.00 and hydrogen was found to be absent.

Di-n-butylmagnesium and Magnesium Hydride. - Magnesium hydride (25 mmole) was prepared by stirring diethylmagnesium (25 mmole) and lithium aluminum hydride (12.5 mmole) in ether at 25° over a period of 2 hours. Magnesium hydride (25 mmole) was stirred with di-s-butylmagnesium (25 mmole) in ether at 25° over a period of 24 hours. The mixture was filtered and the residue dried *in vacuo* over a period of 2 hours. The residue analysis indicated a magnesium:hydrogen ratio of 1.00:1.00. The filtrate analysis indicated a ratio of butane:magnesium:hydrogen of 1.45:1.00:0.81. The infrared spectra of the filtrate gave a broad absorption from 1575 cm^{-1} to 800 cm^{-1} and 775 cm^{-1} to 455 cm^{-1}. The nmr spectra contained several extraneous signals and no interpretation was attempted.

In another experiment, magnesium hydride was prepared as above (25 mmole), filtered and washed with benzene. The magnesium hydride was stirred with di-s-butylmagnesium (25 mmole) in benzene at 25° over a period of 24 hours. The mixture was filtered and the filtrate analysis indicated a magnesium:hydrogen ratio of 1.00:1.00. The filtrate analysis indicated a butane:magnesium:hydrogen ratio of 1.10:1.00:0.97, the aluminum:magnesium ratio was found to be 1.00:6.00. An infrared spectra had broad absorptions at 1320 cm^{-1} to 790 cm^{-1} and 750 cm^{-1} to 450 cm^{-1}. The nmr of the filtrate was not interpretable due to extraneous signals.

Pyrolysis of di-s-butylmagnesium. - s-Butylmagnesium (40 mmole) in benzene was refluxed under nitrogen over a period of 24 hours. A precipitate was formed almost immediately. The precipitate analysis indicated a magnesium:hydride ratio of 1.00:1.96. The filtrate analysis indicated a butane:magnesium:hydrogen ratio of 1.61:1.00:0.15. The nmr spectra was the same as that of di-s-butylmagnesium except [illegible] splitting.

DTA-TGA Analysis of Di-s-butylmagnesium. - DTA-TGA analysis of neat di-s-butylmagnesium (73.98 mg) was carried out at a heating rate of 5°/min. The sample started losing weight almost immediately. An exothermic reaction began at 100°C and terminated at 170°C. The reaction was a two step process. The sample continued to lose weight until magnesium hydride decomposed at 320°.

Results and Discussion

Laboratory prepared lithium hydride failed to react with n-butyl chloride-triethylaluminate in benzene and sodium hydride failed to react with n-butyl chloride in triethylamine.

The pyrolysis of di-s-butylmagnesium produced a small amount of s-butylmagnesium hydride that was soluble in benzene. The major product however was magnesium hydride. The nmr of the filtrate indicated the additional splitting of the s-butyl group could be due to the hydrogen attached to magnesium.

The DTA-TGA indicates one s-butyl group is preferentially cleaved. The energy difference in the two step loss of butyl groups is small and in pyrolysis both groups are removed almost simultaneously, producing only a small amount of s-butylmagnesium hydride.

The best approach found to date is the redistribution of di-s-butylmagnesium and magnesium hydride. Elemental analysis indicates the presence of s-butylmagnesium hydride. The infrared spectra indicate a magnesium-hydrogen stretching band similar to the broad absorption band observed for MgH_2. The n.m.r. was not interpretable due to aluminum contaminants from the synthesis of magnesium hydride by reaction of lithium aluminum hydride and diethylmagnesium which produces lithium tetraethylaluminate as a by-product.

Planned Synthesis. - Further and more precise exploration of the redistribution of the system R_2Mg-MgH_2 will be carried out. Magnesium hydride will be synthesized via hydrogenation of di-s-butylmagnesium in benzene in order to eliminate aluminum contamination. When alkylmagnesium hydrides are isolated, their reactions with olefins to produce new dialkylmagnesium compounds will be carried out. The new unsymmetrical ($RMgR'$) compounds will then be pyrolyzed in attempt to produce new alkylmagnesium hydrides. The molecular association of the new RMgH compounds will be studied.

Other possible routes planned are: the pyrolysis of unsymmetrical dialkyl magnesium compounds in the hope that the energy required to remove one alkyl group will be much greater than the other alkyl group. Reduction of dialkylmagnesium compounds via hydrogenation, dialkylaluminum hydride, and trialkyltin hydride. Reduction of Grignard reagents via hydrogenation and potassium hydride will also be studied.

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Concerning the Existence of HMgX Compounds

By E. C. Ashby,[1] R. A. Kovar, and K. Kawakami

Received July 25, 1969

The preparation of "HMgX" compounds (where X = Cl, Br, and I) by hydrogenolysis and pyrolysis of Grignard compounds in diethyl ether has been previously reported. The authenticity of the "HMgX" product as distinguished from a physical mixture of MgH_2 and MgX_2 was shown by dta-tga analysis, but mainly by X-ray powder pattern data on the basis that the powder patterns for the "HMgX" compounds were different from those of MgH_2 and MgX_2. A repetition of the prior art plus additional work indicates that both hydrogenolysis and pyrolysis of Grignard compounds does not produce HMgX compounds, but a physical mixture of MgH_2 and MgX_2. The reason for the discrepancy was the comparison by prior workers of X-ray powder patterns of "HMgX" compounds containing 0.2–0.3 mol of ether of solvation with ether-free MgH_2 and MgX_2 containing 1.0 mol of ether. When comparison of X-ray powder pattern data was made for the "HMgX" compounds and MgH_2 and MgX_2 containing the same amount of ether of solvation, the "HMgX" compounds were found to exhibit the same X-ray powder lines as those found for a physical mixture of MgH_2 and MgX_2.

Introduction

The hydridomagnesium halides ("HMgX"[2] compounds) represent a novel new class of compounds which presumably can function as a selective reducing agent toward organic substrates[3] and as a starting material toward novel complex magnesium hydrides. The first comprehensive report of the preparation of "HMgX" compounds was made by Wiberg and Strebel[4] in 1957. These workers reported the preparation of crystalline soluble compounds of empirical formula $HMgX \cdot 2O(C_2H_5)_2$ where X = Cl, Br, and I, by the reaction of ethyl Grignard reagents and diborane

$$6C_2H_5MgBr + B_2H_6 \longrightarrow 6HMgBr + 2(C_2H_5)_3B \quad (1)$$

Later we reported[5] that it was not possible to isolate these compounds under the exact conditions described earlier[4] or under a variety of other conditions that might be favorable for forming such compounds. Instead, only chloromagnesium borohydride could be ob-

(1) To whom all inquiries should be sent.

(2) "HMgX" in quotes will be used to represent the product formed from pyrolysis or hydrogenolysis of Grignard compounds which according to this report is actually a mixture of MgH_2 and MgX_2.

(3) R. A. Firestone, *Tetrahedron Letters*, 37, 2625 (1967).

(4) E. Wiberg and P. Strebel, *Ann.*, 607, 9 (1957).

(5) W. E. Becker and E. C. Ashby, *Inorg. Chem.*, 4, 1816 (1965).

tained, regardless of the stoichiometry of the reaction or the mode of reagent addition. The reaction proceeded according to

$$2C_2H_5MgCl + 2H_2 \longrightarrow MgH_2 + MgCl_2 + C_4H_{10} \quad (2)$$

Sometime later, Dymova and Eliseeva[6] reported a second route to "$HMgX$" compounds. This method involved the hydrogenolysis of ethylmagnesium halides ($X = Cl, Br, I$; $R = H$):

$$RCH_2CH_2MgX + H_2 \xrightarrow{5} RCH_2CH_3 + HMgX \quad (3)$$

They found that all of the "$HMgX$" compounds were insoluble in the usual organic solvents and the products contained a nonstoichiometric amount of ether contrary to the results reported earlier by Wiberg and Strebel. They proposed a polymeric structure for the "$HMgX$" compounds. Heating and cooling curves as well as gas evolution polytherms for these compounds were reported and discussed. The "$HMgX$" compounds showed a strong irreversible and endothermic effect at ~125° accompanied by evolution of gas. This transition was assigned to an intramolecular disproportionation of "$HMgX$" to MgH_2 and MgX_2 accompanied by a loss of ether. All subsequent effects in the thermometric analysis at temperatures higher than 125° were consistent with transitions occurring in either MgH_2 or MgX_2 produced in the thermal disproportionation reaction. Thus the conclusion was that "$HMgX$" compounds are formed by the hydrogenolysis of Grignard compounds; however, disproportionation to MgH_2 and MgX_2 occurs at 125°.

At about the same time as the Dymova report, we reported[7] that hydrogenolysis of ether solutions of various Grignard reagents led to the formation of MgH_2 and MgX_2 readily and cleanly. The apparent inconsistency between these two latter reports is resolved when it is realized that we washed all products in the work-up procedure with tetrahydrofuran (eq 4)

$$2HMgX \xrightarrow{THF} MgH_2 + MgX_2 \quad (4)$$

in an attempt to remove the tetrahydrofuran-soluble MgX_2 compounds, while the Russian workers claim that "$HMgX$" compounds disproportionate in tetrahydrofuran. One discrepancy that was not resolved however is the fact that in the cases of hydrogenolysis of RMgBr and RMgI compounds we found that MgH_2 and MgX_2 were indeed formed before tetrahydrofuran washing of the solid since nearly all of the $MgBr_2$ and MgI_2 were found in the diethyl ether solution immediately after hydrogenolysis and prior to washing of the solid with tetrahydrofuran. On the other hand, Russian workers claimed that $MgBr_2$ and MgI_2 were not found in solution but in the solid phase of the reaction mixture. Since $MgCl_2$ is insoluble in diethyl ether we could not, at the time, say that insoluble HMgCl was not initially formed by hydrogenolysis of the RMgCl compound followed by disproportionation of the HMgCl on washing with tetrahydrofuran.[8]

A third route reported to produce "$HMgX$" compounds involves the pyrolysis of Grignard compounds at ~200°. Rice, *et al.*,[9] reported the preparation of nonsolvated $HMgBr$ by pyrolysis of ethylmagnesium bromide. The analysis of the product appeared to be unusually good ($H:Mg:Br = 1.00:1.00:1.00$). These workers cited X-ray powder pattern data (Table V) which were reportedly different from those of MgH_2 and $MgBr_2$. Therefore, it was concluded that $HMgBr$ could not be an equimolar mixture of MgH_2 and $MgBr_2$. Prior to the report by Rice, other workers reported that "$HMgX$" compounds actually exist as equimolar mixtures of hydride and halide.[10,11] These workers based their conclusion primarily on the rapid rate at which magnesium halide is extracted when these products are stirred with THF or ether. However, since Rice, *et al.*, reported that extraction of "$HMgBr$" with dry ether led to *disproportionation* to MgH_2 and $MgBr_2$ followed by *extraction* of the magnesium bromide, the earlier reports were discounted.

The controversial points are as follows. Do "$HMgX$" compounds exist as discrete species differing from equimolar mixtures of magnesium hydride and the corresponding magnesium halide? Does treatment of an "$HMgX$" compound with tetrahydrofuran or diethyl ether result in simple extraction of magnesium halide from the mixture or is magnesium halide extraction preceded by disproportionation of the "$HMgX$" to halide and hydride? Furthermore, if $HMgX$ compounds do exist, are they soluble crystalline compounds containing 2 equiv of ether [$HMgX \cdot 2(C_2H_5)_2O$] as reported by Wiberg or are these compounds insoluble polymeric solids carrying nonstoichiometric amounts of solvent as reported by Dymova? Also, are $HMgX$ compounds subject to thermally induced disproportionation at ~125° as suggested by Dymova or are these species stable when heated to ~200° as suggested by Rice?

Experimental Section

Equipment and Materials.—Manipulation of air-sensitive materials was accomplished by use of standard bench-top techniques and dry nitrogen purge or in a dry box equipped with an atmosphere-purification system for removal of oxygen and moisture.[12] X-Ray powder diffraction data were obtained using a Philips Norelco X-ray unit, using an 11.46-cm diameter camera with Ni-filtered Cu radiation. Exposure times were 6.0 hr for all samples. *d* spacings were evaluated using a precalibrated scale equipped with viewing apparatus. Line intensities were

(6) T. N. Dymova and N. G. Eliseeva, *Russ. J. Inorg. Chem.*, **8**, 850 (1963).

(7) W. E. Becker and E. C. Ashby, *J. Org. Chem.*, **30**, 934 (1961).

(8) It is, of course, quite possible that disproportionation or lack of it could occur depending on the purity of the magnesium used to prepare the Grignard compound. In the present studies triple-sublimed magnesium was used which resulted in the formation of clear and colorless Grignard solutions. Ethylmagnesium bromide prepared from Grignard grade turnings was used. The nature and exact purity of the magnesium used by the Russian workers is not known and therefore could conceivably account for the different observations.

(9) M. J. Rice, Jr., and P. J. Andrulis, Technical Report to the Office of Naval Research, Contract ONR-791(01), 1956.

(10) E. Wiberg and R. Bauer, *Chem. Ber.*, **85**, 593 (1952).

(11) C. Jolibois, *Compt. Rend.*, **166**, 353 (1917).

(12) T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instr.*, **33**, 491 (1962).

TABLE I

HYDROGENOLYSIS OF GRIGNARD REAGENTS

Expt no.	RMgX	Experimental conditions: Concn, M	Pressure, psi	Reaction time, hr	Temp, °C	Product analyses (molar ratio): H	Mg	X	Ether	Halogen recovery from filtrate, %
1	C_2H_5MgCl	1.5	1800-2100	4	125	0.8[illegible]	1.00	1.3[illegible]	0.5[illegible]	7
2[a]	C_2H_5MgBr	1.7	2100-2500	3.5	170	[illegible]	1.00	1.4[illegible]	0.4[illegible]	
3	C_2H_5MgBr	1.0	1900-2300	4	150	1.90	1.00	[illegible]	0.6[illegible]	
4	C_2H_5MgBr	1.0	1800-2100	4	150	1.84	1.00	[illegible]	[illegible]	
5	C_2H_5MgBr	0.5	1800-2000	4	150	[illegible]	1.00	[illegible]	[illegible]	
6	C_2H_5MgBr	1.0	1500-1700	5	125	1.76	1.00	[illegible]	[illegible]	
7	C_2H_5MgBr	1.6	2000	16	125	2.02	1.00	[illegible]	[illegible]	
8	C_2H_5MgBr	1.9	4000-4500	4	100-125	1.90	1.00	[illegible]	[illegible]	
9	C_2H_5MgBr	2.9	1500-3000	5	100	1.82	1.00	[illegible]	[illegible]	
10	C_2H_5MgI	1.0	2000	4	125	1.74	1.00	0.13	0.56	[illegible]
11	C_2H_5MgI	1.0	2000-2100	4	[illegible]	1.2[illegible]	1.00	[illegible]	[illegible]	[illegible]
12	i-C_3H_7MgCl	2.0	3900-4200	12	75	[illegible]	1.00	1.0[illegible]	[illegible]	
13	i-C_3H_7MgCl	2.0	2500-3600	12	75	[illegible]	1.00	1.0[illegible]	[illegible]	4
14	i-C_3H_7MgCl	2.0	1900	4	75	0.77	1.00	1.02	[illegible]	
15	i-C_3H_7MgCl	2.0	1900-2000	4	75	0.72	1.00	[illegible]	[illegible]	
16	i-C_3H_7MgBr	2.0	2000	3.5	75	[illegible]	1.00	[illegible]	[illegible]	
17	i-C_3H_7MgBr	[illegible]	3400-3900	17.5	75	[illegible]	1.00	[illegible]	[illegible]	[illegible]
18	i-C_3H_7MgI	1.0	4500-4700	12	75	[illegible]	1.00	[illegible]	[illegible]	[illegible]
19	t-C_4H_9MgCl	0.5	3300	5	150	[illegible]	1.00	1.02	[illegible]	

[a] Almost all of the ether was gone. No X-ray powder pattern was obtained.

estimated visually. Nuclear magnetic resonance spectra were obtained using a Varian Associates Model A-60 spectrometer (benzene internal standard). Fisher Certified reagent grade ethyl bromide, ethyl iodide, isopropyl chloride, isopropyl bromide, isopropyl iodide, and t-butyl [illegible] were distilled over P_2O_5 prior to use. Ethyl chloride was distilled over molecular sieve 4A before use. Mallinckrodt anhydrous ether was further purified by distillation over $LiAlH_4$. All Grignard compounds were prepared using Dow triply sublimed magnesium.[12]

Preparation of Grignard Reagents.—Grignard reagents were prepared as described previously.[3] All Grignard reagents were filtered in a dry nitrogen box producing clear, colorless solutions. Magnesium was determined by Versene titration and halogens were determined by the Volhard method. In all cases the magnesium and halogen analyses indicated a magnesium to halogen ratio of 1.0:1.0 to within [illegible], with the exceptions of i-C_3H_7MgBr, i-C_3H_7MgI, and t-C_4H_9MgI which contained [illegible] excess magnesium halide (Table VII). t-Butylmagnesium chloride-ether which is dimeric in benzene solution[14] was prepared from a solution of t-butylmagnesium chloride in ether into which excess dry benzene had been distilled. Codistillation of the ether left the desired compound in solution. The Mg to Cl ratio was 1:1. The proton magnetic resonance spectrum of this benzene solution revealed three signals at 2[illegible] (quartet), [illegible] (singlet), and [illegible] (triplet) Hz above the benzene signal of area ratio [illegible], [illegible], and 6[illegible], respectively. These signals are assigned to ether methylene, t-butyl, and ethyl methyl, respectively.

$C_2H_5MgBr \cdot 2O(C_2H_5)_2$ was isolated by the method reported earlier.[15] Confirmation of this species was obtained from the proton magnetic resonance spectrum which showed ether methylene quartet, ether methyl triplet, $MgCH_2CH_3$ quartet, and $MgCH_2CH_3$ triplet signals at 2[illegible], [illegible], 4[illegible], and [illegible] Hz above the benzene internal reference. The relative area ratio of the ether methylene and $MgCH_2CH_3$ signals was [illegible].

Hydrogenolysis Procedure.—Two different reaction conditions were used based on the previous reports[4,5] (Table I). In one,[4] a [illegible] aliquot of a [illegible] M ether solution of ethyl Grignard reagent was charged into a [illegible]-ml Magne-Dash autoclave. The mixture was heated to 1[illegible], 1[illegible], and 1[illegible]° for [illegible] hr under 1[illegible]-2[illegible] psi of hydrogen. In another procedure,[5] a [illegible], [illegible], or [illegible]-ml aliquot of a [illegible] M ether solution of isopropyl Grignard reagent was heated to [illegible]° for [illegible] hr under [illegible] psi of hydrogen. After the reaction mixture had been cooled and vented, it was filtered in the drybox. Both the precipitate, after drying under vacuum at [illegible]° for [illegible] hr, and the filtrate were analyzed for magnesium and halogen as mentioned above. Analysis for hydridic hydrogen, where applicable, was accomplished by measuring the gas evolved upon hydrolysis of a weighed sample. The presence of ether was confirmed by hydrolyzing a weighed sample in excess benzene diluted using a measured amount of [illegible] vol % H_2SO_4. The ether released into the benzene was then analyzed by gas liquid partition chromatography. Typical hydrogenolysis experiments are as follows.

Ethylmagnesium Chloride.—Ethylmagnesium chloride ([illegible] mol in [illegible] ml of ether) was charged into a [illegible]-ml Magne-Dash autoclave. The mixture was heated at 1[illegible]° for 4 hr under 1[illegible]-2[illegible] psi of hydrogen. After the reaction mixture had been cooled and vented, it was filtered in a drybox. The white voluminous precipitate was dried under vacuum at [illegible]° for [illegible] hr and analyzed. The H:Mg:Cl:ether ratio of [illegible] shows that the product has the empirical formula $HMgCl \cdot [O(C_2H_5)_2]_{[illegible]}$. The filtrate was found to contain some [illegible] unreacted ethylmagnesium chloride.

Ethylmagnesium Bromide.—Ethylmagnesium bromide ([illegible] mol in 1[illegible] ml of ether) was heated at 1[illegible]° for 4 hr under 1[illegible]-2[illegible] psi of hydrogen. The white insoluble solid contained H, Mg, Br, and ether in the ratio of 1.8[illegible]:1.00:[illegible]:[illegible]. The filtrate showed two layers. Analyses of the [illegible] layer showed an Mg:Br ratio of 1.[illegible]:1.[illegible].

Isopropylmagnesium Chloride.—Isopropylmagnesium chloride ([illegible] mol in 1[illegible] ml of ether) was heated at [illegible]° for [illegible] hr under 2[illegible]-3[illegible] psi of hydrogen. Twenty grams [illegible] of the white voluminous precipitate contained an H:Mg:Cl:ether ratio of [illegible]:1.00:1.[illegible]:[illegible]. Its X-ray powder pattern is almost exactly the same as that of the [illegible] product of ethylmagnesium chloride. The filtrate contained unreacted [illegible] isopropylmagnesium chloride.

Isopropylmagnesium Bromide.—Isopropylmagnesium bromide ([illegible] mol in [illegible] ml of ether) was heated at [illegible]° for [illegible] hr under

(12) Ethylmagnesium bromide prepared from Grignard grade magnesium turnings was subjected to hydrogenolysis in one attempt to prepare an authentic HMgBr compound with results analogous in every respect to those reported for hydrogenolysis of ethylmagnesium bromide prepared from triply sublimed magnesium. Conclusions reached in this paper are thus valid for Grignard compounds prepared from these two grades of magnesium.

(14) G. E. Coates and J. A. Heslop, *J. Chem. Soc.*, *A*, [illegible] (1966).

(15) E. J. Gaspardo[illegible] and R. E. Randle, *J. Am. Chem. Soc.*, **86**, [illegible] (196[illegible]).

TABLE II

PYROLYSIS OF GRIGNARD REAGENTS

Expt no.	RMgX	Experimental conditions: Temp, °C	Reaction time, hr	Pressure, mm	Atomic molar ratio: H	Mg	X	Ether[a]
1	$C_2H_5MgBr \cdot 2(O(C_2H_5)_2)$	200	2	1	0.88	1.00	1.00	0.08
2	C_2H_5MgBr	195	22	3	0.56	1.00	0.99	0.26
3		195	18	1	0.51	1.00	0.99	0.31
4		195	6	3	0.39	1.00	1.00	0.34
5		150	5	3	0.53	1.00	0.98	0.44
6	i-C_3H_7MgCl	140	4	3	0.74	1.00	1.02	0.15
7		140	2.5	4	0.74	1.00	1.08	0.05
8		140	1	2	0.71	1.00	1.12	0.01
9		140	0.5	4	0.67	1.00	1.05	0.12
10		130	17	3	0.69	1.00	0.95	0.01
11		130	10	5	0.54	1.00	1.20	0.13
12		130	6	3	0.83	1.00	1.07	0.03
13		130	6	5	0.79	1.00	1.04	0.04
14		130	4	3	0.80	1.00	1.03	0.08
15		130	2	2	0.61	1.00	1.00	0.31
16		130	1	4	0.51	1.00	1.05	0.33
17		110	72	3	0.84	1.00	1.05	0.33
18		110	16	5	0.78	1.00	1.04	0.13
19		110	5	5	0.73	1.00	0.99	0.17
20	i-C_3H_7MgBr	160	5.5	1	0.83	1.00	1.07	0.04
21		140	6	1	0.81	1.00	1.09	0.09
22		130	6	3	0.72	1.00	1.08	0.21
23		120	6	1	0.56	1.00	1.07	0.34
24		110	24	3	0.65	1.00	1.07	0.26
25	i-C_4H_9MgI	150–160	1½	0.5	0.49	1.00	1.12	
26		150–160	2½	0.5	0.56	1.00	1.20	
27		160–170	1	1	0.75	1.00	1.08	0.162
28		170	1	1	0.78	1.00	1.06	0.802
29		170	2	1	0.74	1.00	1.06	
30		180	1	1	0.76	1.00	1.05	0.245
31		205	1	1	0.70	1.00	1.06	1.34

[a] Ether by difference.

3460–3800 psi of hydrogen. The white compact precipitate contained an H:Mg:Br:ether ratio of 1.88:1.00:0.07:0.03. The filtrate contained 0.19 g-atom of Mg and 0.28 g-atom of Br.

Dimeric *i*-Butylmagnesium Chloride–Ether in Benzene.—*i*-Butylmagnesium chloride:ether (0.075 mol in 150 ml of benzene) was heated at 150° for 5 hr under 3500 psi of hydrogen. The gray-white precipitate which formed contained an H:Mg:Cl:ether ratio of 0.96:1.0:1.02:0.05.

Pyrolysis Procedure.—A number of experiments were carried out in order to determine the best combination of reaction temperature and time needed to produce a pure HMgX product. Typical results are shown in Table II. A typical procedure for pyrolysis of Grignard reagents follows.

Grignard reagents in ether were charged into a 200-ml round-bottom flask containing a large "egg shape" stirring bar. The ether was removed under vacuum at 50°. The Grignard solution gradually became viscous during the ether solvent removal process until finally the stirrer could not move. At this stage, the stirrer was made to move by occasional shaking of the flask while the temperature was increased to the reaction temperature. Pyrolytic reactions of ethyl- and isopropylmagnesium bromide and isopropylmagnesium chloride were carried out in this way.

In another procedure, the ether was removed under vacuum at 50° until the stirring bar stopped moving. Nujol was added and the mixture was heated to 90° for a prolonged time (120 hr) to ensure complete removal of solvated ether. The temperature was raised gradually to the point where pyrolysis was carried out over a period of 1 hr. Isobutylmagnesium iodide was pyrolyzed in this way. A white product instead of a gray one was obtained.

Extraction Experiments.—A 2.684-g sample of solid produced by the hydrogenolysis of C_2H_5MgCl in diethyl ether (H:Mg:Cl:ether = 0.84:1.00:1.07:0.36) was stirred in 50 ml of dry THF for 3 min. The mixture was filtered quickly and 0.42 g of a white solid was obtained. The solid product and the filtrate were analyzed. The solid contained an H:Mg:Cl ratio of 1.77:1.00:0.10 and its X-ray powder pattern showed lines for only MgH_2. The filtrate contained 99 and 62% of the original amount of Cl and Mg, respectively. Experiments using "HMgCl," "HMgBr," and "HMgI" prepared from pyrolysis reactions gave similar results which are shown in Table III.

Synthesis and Stepwise Desolvation of $MgCl_2$, $MgBr_2$, and MgI_2.—$MgCl_2 \cdot O(C_2H_5)_2$ was prepared from the reaction of isopropylmagnesium chloride and HCl in diethyl ether. Dropwise addition of a stoichiometric quantity of HCl to the stirred Grignard solution under nitrogen purge resulted in precipitation of the halide containing an Mg:Cl:ether ratio of 1.00:1.98:1.02. Stepwise desolvation was accomplished by heating this material under vacuum for different periods of time and at different temperatures. Heating for 1 hr at room temperature produced a material with a Mg to ether ratio of 1.00:0.77. This ratio was found to be 1.00:0.5, 1.00:0.28, 1.00:0.09, and 1.00:0.01 when this material was heated for 1-hr periods at 50, 75, 100, and 125°, respectively. The ratio of magnesium to chlorine was found to be 1:1.98 in the completely desolvated material. Magnesium bromide–ether and magnesium iodide–2-ether were prepared by the reaction of the appropriate mercuric halide with triply sublimed magnesium metal in ether solution.[16] Magnesium to halide ratios were found to be 1:1.98 and 1:1.97, respectively. Stepwise desolvation was accomplished as above for magnesium chloride.

Preparation of MgH_2. A. Reaction of $LiAlH_4$ with Diethyl-

(16) E. C. Ashby and R. C. Arnott, *J. Organometal. Chem.* (Amsterdam), 14, 1 (1968).

TABLE III
RESULTS OF EXTRACTION OF "HMgX" PRODUCTS

Compound	Solvent	Atomic ratio of original compound H	Mg	X	Analysis of residue, atomic ratio H	Mg	X	Analysis of soln, % Mg	X
Hydrogenolysis HMgCl[a]	THF	0.84	1.00	1.07	1.77	1.00	0.10	62	90
Pyrolysis HMgCl[a]	THF	0.79	1.00	1.09	1.02	1.00	0.73	49	60
Pyrolysis HMgBr[a]	Ether	0.83	1.00	1.07	1.68	1.00	0.13	43	78
Pyrolysis HMgI	Ether	0.73	1.00	1.09	1.43	1.00	0.07		

[a] X-Ray powder pattern of residues of these cases show lines only for MgH_2.

magnesium.[17]—Diethylmagnesium (0.1 mol) in diethyl ether from 0.1 mol of diethylmercury and excess magnesium[16] was allowed to react with 0.45 mol of $LiAlH_4$ in diethyl ether. Precipitation of MgH_2 was noted with addition of the first drops of hydride. The mixture was stirred for 3 days after completion of the addition and then filtered in the drybox. The precipitate was washed three times with diethyl ether to remove any excess diethylmagnesium followed by vacuum drying at room temperature for 1 hr. The magnesium to hydrogen ratio was found to be 1.00:1.92.

B. Reduction of Diethylmagnesium with Hydrogen at Elevated Temperatures.—Diethylmagnesium (0.1 mol in 150 ml of ether) was charged into an autoclave and heated under 2000 psi of hydrogen at 75° for 10 hr. The precipitate which had formed was filtered in the drybox and washed three times with diethyl ether. The magnesium to hydrogen ratio was found to be 1.00:1.91.

C. Pyrolysis of Diethylmagnesium.—Diethylmagnesium (0.05 mol) was heated for 2-hr periods at 100, 150, 200, and 220°. Infrared analysis (Nujol mull) of these materials indicated only partial pyrolysis after heating at 200° for 2 hr. All of the diethylmagnesium had been pyrolyzed by heating for 2 hr at 220°. The yield was 0.98 g of a yellow-brown material violently explosive upon exposure to the atmosphere. The magnesium to hydrogen ratio was found to be 1.00:1.94.

Results and Discussion

Our evaluation of the reaction of ethyl Grignard compounds with diborane as a route to HMgX compounds was reported earlier.[5] We were not able to prepare HMgX compounds by this method under any conditions including the exact conditions stated by Wiberg and Strebel in their earlier report. It was clearly demonstrated that the products of this reaction in tetrahydrofuran under a variety of conditions are the halogenomagnesium borohydride ($XMgBH_4$) and triethylborane (eq 2).

The two other methods reported for the preparation of HMgX compounds involve hydrogenolysis and pyrolysis of Grignard compounds. Dymova, *et al.*,[6] claimed to have prepared HMgCl, HMgBr, and HMgI containing 0.1–0.9 mol of solvated ether by the hydrogenolysis of ethyl Grignard compounds in diethyl ether. Rice, *et al.*,[9] claimed to have prepared HMgBr by the pyrolysis of ethyl- and *t*-butylmagnesium bromides at 190 and 200°, respectively. Since the "HMgX" compounds were stated by the Russian workers to disproportionate in tetrahydrofuran,[6] it was clear that this solvent was to be avoided especially in the hydrogenolysis experiments in which the Grignard compounds are allowed to react with hydrogen in solution. It also appeared clear that the Russian work[6] had to be repeated since the hydrogenolysis experiments were performed in diethyl ether whereas earlier Rice reported that "HMgX" compounds disproportionate in diethyl ether.[9] Furthermore the pyrolysis studies of Rice[9] had to be repeated since the Russian workers claimed that "HMgX" compounds disproportionate on heating to 125°[6] and Rice reported the preparation of "HMgX" compounds by pyrolysis of Grignard compounds at 200°.[9] As a starting material for hydrogenolysis and pyrolysis reactions, ethyl-, isopropyl-, and isobutylmagnesium halides were chosen. Isopropyl compounds were chosen because earlier we had shown that isopropylmagnesium chloride reacts with hydrogen at a faster rate than any other Grignard compounds investigated at the time.[7] Thus lower reaction temperatures could be used to effect hydrogenolysis of the isopropyl Grignard reagent which presumably would lead to a purer product. Isobutyl compounds were investigated since triisobutylaluminum is known to undergo hydrogenolysis and pyrolysis readily compared to other aluminum alkyls. The ethyl Grignard compounds were investigated because previous workers used these compounds for both hydrogenolysis and pyrolysis studies and it was considered necessary to repeat this work.

Previous workers employed elemental analysis but particularly powder diffraction and dta–tga analysis of reaction products in order to determine whether the product was a single compound, HMgX, or a mixture of MgH_2 and MgX_2. Powder diffraction and dta–tga analytical evaluation of the product are crucial since the reported "HMgX" compounds are insoluble in diethyl ether and are said to disproportionate in tetrahydrofuran. It was by evaluation of both X-ray powder diffraction and dta–tga data that both Russian and American workers decided that the products of hydrogenolysis and pyrolysis of Grignard compounds produced "HMgX" compounds and not mixtures of MgH_2 and MgX_2.

Pyrolysis of Grignard reagents yielded materials which contain hydridic hydrogen, magnesium, halide, and ether in the approximate ratio $1:1:1:n$, where $n << 1$. As can be seen from Table II the hydrogen content of the product was usually low presumably due to decomposition of the product during heating. The pyrolytic reactions were not markedly temperature or time dependent; however, as expected, pyrolysis was effected under much milder conditions and with shorter reaction times when the alkyl group was isopropyl or isobutyl. The nature of the pyrolytic product was independent of the alkyl group as demonstrated

(17) G. Barberas, C. Dillard, A. Finholt, T. Wartik, K. Wilzbach, and H. Schlesinger, *J. Am. Chem. Soc.*, 73, 4585 (1951).

TABLE IV

X-RAY POWDER PATTERN *d*-SPACING DATA. HYDROGENOLYSIS AND PYROLYSIS OF GRIGNARD COMPOUNDS

"HMgCl" (hydrogenolysis)	"HMgCl" (hydrogenolysis, heated at 120° for 2 hr)	"HMgCl" (pyrolysis)	"HMgBr" (pyrolysis)	"HMgI" (pyrolysis)
12.3 m	5.9 s	6.0 s	6.3 m	3.6 vw
9.3 s	2.92 s	3.2 vw	3.28 w	3.4 m
7.2 m	2.76 s	3.1 vw	3.10 m	3.15 s
6.3 vw	2.60 s	2.98 s	2.90 s	2.48 m
5.5 vw	2.50 vw	2.79 w	2.68 w	2.08 m
4.75 vw	1.80 s	2.60 s	2.49 vw	1.93 m
3.19 w	1.73 w	2.52 w	2.26 m	1.78 m
2.76 vw	1.67 vw	2.43 vw	1.90 s	1.74 w
2.50 vw		2.27 vw	1.82 vw	1.72 w
2.35 vw		2.02 vw	1.76 w	1.60 vw
2.13 vw		1.83 s	1.66 vw	1.56 vw
1.82 vw		1.75 w	1.62 m	1.42 vw
1.67 vw		1.69 w	1.59 w	1.34 w
		1.56 w	1.56 w	1.33 w
		1.49 w	1.225 m	1.29 vw
			1.20 m	1.27 vw
				1.20 vw
				1.17 vw
				1.13 vw
				1.10 vw

by the fact that the powder diffraction patterns obtained from the products of pyrolysis of ethylmagnesium bromide and isopropylmagnesium bromide were identical. Analogous results were obtained for the chloro and iodo Grignard compounds. Furthermore, the X-ray powder diffraction pattern obtained from the pyrolysis product of the bromo Grignard compounds contains almost all of the lines reported earlier (Tables IV and V) for the pyrolysis of ethylmagnesium bromide,[9] indicating identical products.

In order to determine whether the "HMgX" products exist as an authentic single compound or as equimolar mixtures of hydride and halide, the X-ray powder diffraction patterns of these products were compared with the powder diffraction patterns for magnesium hydride and MgX_2 (X = Cl, Br, and I). Powder diffraction data for MgH_2 synthesized by different routes (see Experimental Section) was compiled since the reactivity of each MgH_2 is sensitive to the synthetic route and it was felt that differences in reactivity might be due to differences in structure, although a contrary explanation to this phenomenon has appeared.[18] Powder diffraction patterns for MgH_2 produced from the various different synthetic routes were found to be identical with the exception that in the case of the reduction of a dialkylmagnesium compound with $LiAlH_4$ or with hydrogen at elevated temperature the lines were broader and more diffuse than for MgH_2 produced in the other reactions. A representative MgH_2 spectrum is recorded in Table V. X-Ray powder diffraction data were compiled for solvated MgX_2, MgX_2 of intermediate solvation, and desolvated MgX_2, since the diffraction patterns are expected to be sensitive to changes in coordination about magnesium. It was initially thought most meaningful to compare the diffraction data for the pyrolytic "HMgX" products which contain relatively small amounts of coordinated ether with the diffraction patterns of the magnesium halides which contain little or no coordinated ether. Powder diffraction patterns for the magnesium halides were markedly sensitive to the degree of coordination and are summarized in Table VI.

From comparison of the data listed in Tables IV and VI it can be concluded that all of the lines present in the spectra of the desolvated magnesium halides are present in the spectra of the corresponding pyrolytic "HMgX" product. The spectrum of "HMgI" contains

TABLE V

X-RAY POWDER PATTERN *d*-SPACING DATA. MgH_2 AND "HMgX" COMPOUNDS

MgH_2	"HMgCl" (hydrogenolysis of $(t\text{-}C_4H_9)MgCl\cdot O(C_2H_5)_2$)	"HMgBr" (pyrolytic product of C_2H_5MgBr by Rice[9])
3.19 vs	6.0 s	5.51
2.76 vw	3.18 m	3.30
2.495 vs	3.05 m	2.94 s
2.24 m	2.94 s	2.12
1.67 s	2.75 m	1.91 s
1.59 m	2.55 vs	1.65
1.50 w	2.48 m	1.61
1.42 w	2.24 m	1.22
1.36 w	1.97 m	1.16
1.335 w	1.80 s	
1.246 w	1.72 m	
1.15 w	1.66 m	
1.125 w	1.59 w	
	1.54 m	
	1.45 m	
	1.42 w	
	1.36 w	
	1.34 w	
	1.28 w	
	1.25 w	
	1.17 w	
	1.14 m	
	1.04 m	

TABLE VI

X-RAY POWDER PATTERN *d*-SPACING DATA. MgX_2 COMPOUNDS

$MgCl_2(O(C_2H_5)_2)_n$ n = 1	$MgCl_2(O(C_2H_5)_2)_n$ n = 0.27	$MgCl_2(O(C_2H_5)_2)_n$ n = 0	$MgBr_2\cdot(O(C_2H_5)_2)_2$	$MgBr_2$	$MgI_2\cdot(O(C_2H_5)_2)_2$	MgI_2
10.5 vw	12.4 s	5.8 s	8.0 s	6.2 m	8.0 m	3.5 w
9.5 vw	9.2 s	3.05 w	7.3 s	3.27 w	6.90 m	3.38 m
7.8 vw	7.2 m	2.94 s	5.7 vw	3.10 m	6.10 w	3.13 s
6.3 w	6.2 w	2.75 m	5.3 w	2.89 s	5.80 vw	2.46 m
6.0 w		2.55 s	4.40 vw	2.68 w	5.20 m	2.05 m
5.6 w	5.5 w	2.45 w	3.95 vw	2.26 m	4.30 w	1.92 m
2.9 w	4.8 w	2.32 w	3.55 s	1.90 s	3.94 vw	1.76 m
2.5 w	2.75 w	2.13 m	3.92 vw	1.82 w	3.88 vw	1.73 m
2.56 w	2.30 w	1.95 w	3.24 m	1.76 w	3.80 w	1.70 m
1.80	2.10 w	1.80 s	3.18 vw	1.63 m	3.66 w	1.58 w
	1.80 w	1.72 m	2.98 m	1.59 w	3.43 m	1.53 vw
		1.65 w	2.86 vw	1.56 w	3.31 w	1.405 vw
		1.54 m	2.75 vw	1.46 vw	3.20 w	1.325 m
		1.51 w	2.62 vw	1.30 vw	3.05 w	1.315 m
		1.47 m	2.51 w	1.225 m	2.86 vw	1.275 vw
		1.43 w	2.39 w	1.205 m	2.75 vw	1.255 w
		1.37 w	2.29 vw	1.16 w	2.64 vw	1.195 w
		1.33 w	2.13 vw	1.10 w	2.48 w	1.165 w
		1.27 w	2.07 vw		2.38 vw	1.125 w
		1.14 m	1.90 w		2.33 vw	1.085 w
		1.04 m	1.84 vw		2.26 vw	1.035 w
		0.98 m	1.73 vw		2.20 vw	
		0.905 w	1.61 vw		2.13 vw	
			1.58 vw		2.09 vw	
					2.06 vw	
					1.93 vw	

(18) K. M. Mackay, "Hydrogen Compounds of the Elements," Wilmer Bros. Ltd., Birkenhead, Cheshire, England, 1966, p 11.

only the lines present in desolvated MgI_2 while the spectra of "HMgCl" and "HMgBr" contain lines present in desolvated $MgCl_2$ and $MgBr_2$, respectively, and additional relatively weak lines which correspond exactly to the strongest lines present in a pure sample of MgH_2. These are the results expected for an equimolar mixture of MgH_2 and MgX_2 since equimolar mixtures of hydride and halide contain a relatively low weight percentage of hydride owing to the relatively low molecular weight of this component. Furthermore, the weight percentage of MgH_2 present in equimolar mixtures of hydride and halide is expected to decrease in the series where halide = Cl, Br, and I, and lines due to MgH_2 might be impossible to detect in an equimolar mixture of MgH_2 and MgI_2. This was confirmed from analysis of the powder diffraction spectrum of an authentic 1:1 molar mixture of MgH_2 and MgI_2, while weak lines due to MgH_2 could be detected in authentic 1:1 molar mixtures of MgH_2 and MgX_2 (X = Cl and Br). The X-ray powder patterns for the authentic 1:1 molar mixtures of MgH_2 and MgX_2 (X = Cl, Br, and I) were identical with the corresponding pyrolytic HMgX product, and thus it must be concluded that these materials exist as equimolar mixtures.

Essentially all of the $MgCl_2$ was extracted into solution when pyrolytic "HMgCl" was stirred with excess, dry THF for 3 min (Table III), while $MgBr_2$ and MgI_2 were readily extracted when pyrolytic "HMgBr" and "HMgI," respectively, were stirred with excess, dry diethyl ether for a period of 3 min. X-Ray powder patterns of the undissolved solids were identical with that of MgH_2.

We were not able to isolate HMgX compounds (where X = Br and I) by hydrogenolysis of Grignard compounds in diethyl ether. Twelve hydrogenolysis experiments were carried out in which several Grignard compounds were allowed to react under a variety of conditions (varying the temperature, pressure, and concentration), including those specified by the Russian workers.[6] Under all conditions, when the Grignard compound was a bromide or iodide, a white solid was formed which was shown by both elemental and X-ray powder analysis to be predominantly MgH_2. The filtrate contained almost all of the initial halide (Table I). Hydrogenolysis of both ethyl- and isopropylmagnesium chlorides in ether produced a white, insoluble product which contained hydrogen, magnesium, chlorine, and ether in the approximate ratio of $1:1:1:n$ (where $n < 1$). This result is to be expected since $MgCl_2$ is insoluble in diethyl ether. Thus the solid product could be HMgX or a mixture of MgH_2 and MgX_2. The results in Table I show that the hydrogen content of the product was always slightly low and the chlorine content slightly high. The X-ray powder pattern of the product from ethyl- and isopropylmagnesium chlorides showed similar lines, indicating that the same product is formed from hydrogenolysis of these Grignard compounds. Very few of these lines were in common with the X-ray

TABLE VII
ANALYSES OF GRIGNARD SOLUTION

Grignard	Conen, M		Mg:X	% MgX_2
	Mg	X		
C_2H_5MgBr	1.74	1.70	1.000:0.977	2
i-C_3H_7MgCl	0.361	0.365	1.000:1.011	1
i-C_3H_7MgCl	2.55	2.61	1.000:1.024	2
C_2H_5MgBr	3.88	3.85	1.000:0.992	1
C_2H_5MgBr	3.64	3.65	1.000:0.997	1
i-C_3H_7MgCl	2.48	2.50	1.000:1.000	0
i-C_3H_7MgCl	1.99	2.09	1.000:1.050	5
i-C_3H_7MgBr	1.92	2.04	1.000:1.062	6
C_2H_5MgCl	3.58	3.60	1.000:1.009	1
C_2H_5MgI	3.54	3.44	1.000:0.972	2
i-C_3H_7MgI	1.07	1.26	1.000:1.178	18
i-C_3H_7MgI	1.001	1.125	1.000:1.118	12
i-C_3H_7MgI	0.894	1.07	1.000:1.200	20
i-C_3H_7MgI	0.206	0.251	1.000:1.218	21
i-C_3H_7MgCl	1.714	1.724	1.000:1.007	1
i-C_3H_7MgBr	0.812	0.823	1.000:1.014	1
i-C_3H_7MgI	0.594	0.629	1.000:1.059	6

powder patterns of $MgCl_2 \cdot O(C_2H_5)_2$ and desolvated $MgCl_2$ indicating either an authentic HMgCl compound or an intermediate degree of coordination on $MgCl_2$ (Tables IV and VI). Several lines are present, however, which can be assigned to MgH_2 (Table V). Two experiments were conducted in order to decide between these possibilities. A sample of the hydrogenolysis "HMgCl" was heated under vacuum at 120° for a period of 2 hr to remove coordinated ether. None of the characteristic ether bands was present in the infrared spectrum of this heated material and the X-ray powder pattern (Table IV) showed strong lines identical with those in desolvated $MgCl_2$ and weak lines identical with the lines in X-ray powder spectra of pure MgH_2, indicating an equimolar mixture of MgH_2 and $MgCl_2$. Desolvation of HMgCl at 120°, however, could have been accompanied by an intramolecular disproportionation to MgH_2 and $MgCl_2$ suggested earlier by Dymova, *et al.*[6] We therefore compared the X-ray powder patterns of hydrogenolysis "$HMgCl \cdot (O(C_2H_5)_2)_n$" (where n = 0.9-0.3) with powder diffraction data for $MgCl_2 \cdot (O(C_2H_5)_2)_n$ (where n = 0.9-0.3). We found that spectra obtained for $MgCl_2$ of intermediate solvation were very similar to spectra of hydrogenolysis "HMgCl" (compare, for example, the spectra of hydrogenolysis "HMgCl" and of $MgCl_2$ containing 27 mol % $O(C_2H_5)_2$, Tables IV and VI) with the exception that lines attributable to MgH_2, present in the latter spectrum, are not present in the former spectra. We, therefore, conclude that the hydrogenolysis "HMgCl" consists of an equimolar mixture of MgH_2 and $MgCl_2$. Essentially all of the chloride goes into solution when this material is stirred with excess, dry THF for 3 min. During this period the composition of the solid changed markedly. X-Ray and elemental analyses indicated that the insoluble residue is MgH_2 (Table III).

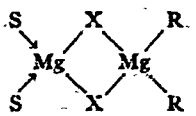
It was of some concern that the nature of the product formed in the hydrogenolysis or pyrolysis of Grignard compounds would depend to a large extent on the composition of the Grignard compound in solution (Table VII) (hydrogenolysis) or the solid-state struc-

ture (pyrolysis). For example RMgX species would be expected to form HMgX, and $R_2Mg \cdot MgX_2$ species would be expected to form a mixture of MgH_2 and MgX_2

$$2RMgX \longrightarrow HMgX$$

$$R_2Mg + MgX_2 \longrightarrow MgH_2 + MgX_2$$

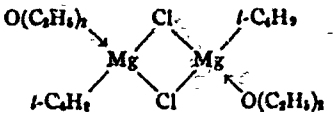
Therefore it seemed worthwhile to pyrolyze a Grignard compound that was known to possess the RMgX solid-state structure. In this connection the bis(diethyl ether) adduct of ethylmagnesium bromide was isolated prior to pyrolysis since earlier[19] it had been demonstrated that this species exists as an RMgX compound with each magnesium atom bonded to one bromine and one alkyl group. It had also been suggested that simple removal of solvent from a Grignard compound, as in vacuum distillation, results in precipitation of a material containing unsymmetrically bridged alkyl and halogen groups which should result on pyrolysis in the formation of a mixture of MgH_2 and MgX_2.



A material containing hydrogen, magnesium, and bromine in the ratio 0.88:1.00:1.06 (Table II) was obtained when the bis(diethyl ether) adduct of ethylmagnesium bromide was heated at 200° for 2 hr. The X-ray powder pattern of this material was identical with the patterns obtained from pyrolysis of other bromo Grignard compounds indicating that a mixture of MgH_2 and $MgBr_2$ was again obtained.

(19) L. J. Guggenberger and R. E. Rundle, *J. Am. Chem. Soc.*, 86, 5344 (1964).

The 1:1 etherate adduct of *t*-butylmagnesium chloride, which is dimeric in benzene, was hydrogenated since earlier[14] it had been suggested that this compound exists in benzene solution as the symmetrically bridged dimer



Hydrogenolysis of this Grignard compound resulted in precipitation of a gray, white solid containing very little ether (essentially all of the diethyl ether is present in the benzene) and hydrogen, magnesium, and chloride in a ratio of 0.91:1.00:1.02. The X-ray powder pattern of this material (Table V) is identical with the pattern obtained for an authentic 1:1 molar mixture of MgH_2 and $MgCl_2$ and, therefore, this material also exists as a mixture.

In conclusion, we were not able to prepare HMgX compounds (X = Cl, Br, or I) from either pyrolysis or hydrogenolysis of Grignard reagents under a variety of reaction conditions. In contrast to earlier reports by Russian, German, and American workers, the products of these reactions were shown, by careful comparison of appropriate X-ray powder diffraction data, to consist of mixtures of MgH_2 and the corresponding MgX_2. Reduction of an RMgX compound to HMgX by the reactions described in this study must necessarily follow immediately with formation of mixtures of hydride and halide.

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Concerning the Preparation of Magnesium Aluminum Hydride. A Study of the Reactions of Lithium and Sodium Aluminum Hydrides with Magnesium Halides in Ether Solvents

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The reactions of alkali metal aluminum hydrides with magnesium halides in ether solvents were investigated as possible routes to magnesium aluminum hydride [$Mg(AlH_4)_2$]. The ability of these reactions to produce $Mg(AlH_4)_2$ depended on the nature of the alkali metal, the halide, the solvent, and the solubility of the alkali metal halide by-product. Contrary to previous reports $Mg(AlH_4)_2$ could not be prepared by the reaction of $LiAlH_4$ and magnesium bromide in diethyl ether. This reaction regardless of the nature of the halogen or solvent was found to produce an equilibrium mixture ($LiAlH_4 + MgBr_2 \rightleftharpoons LiBr + BrMgAlH_4$) which varied in its composition depending on the amount of $LiAlH_4$ used but which did not contain any detectable amount of $Mg(AlH_4)_2$. Magnesium aluminum hydride was prepared in a pure form as the ether solvate by the reactions of $NaAlH_4$ and $MgCl_2$ in tetrahydrofuran and $NaAlH_4$ and $MgBr_2$ in diethyl ether. Magnesium aluminum hydride is insoluble in both diethyl ether and tetrahydrofuran; thus it was separated from the NaCl and NaBr by-products by Soxhlet extraction. Because of the solubility of NaI in tetrahydrofuran, $Mg(AlH_4)_2$ as the tetrakis(tetrahydrofuran) solvate was prepared halogen free by the reaction of sodium aluminum hydride and magnesium iodide. Halogenomagnesium aluminum hydrides ($XMgAlH_4$, where X = Cl and Br) were prepared in tetrahydrofuran by the reaction of sodium aluminum hydride and the magnesium halide in 1:1 stoichiometry. Infrared spectra and powder diffraction data are presented for all of the compounds prepared.

Introduction

The preparation of magnesium aluminum hydride ($Mg(AlH_4)_2$) was first reported in 1950 by Wiberg and Bauer.[2-4] The preparation of this new hydride was reported by three different synthetic routes represented by eq 1-3. Magnesium hydride (MgH_2) was reported

$$4MgH_2 + 2AlCl_3 \longrightarrow Mg(AlH_4)_2 + 3MgCl_2 \quad (1)$$

$$MgH_2 + 2AlH_3 \longrightarrow Mg(AlH_4)_2 \quad (2)$$

$$2LiAlH_4 + MgBr_2 \longrightarrow Mg(AlH_4)_2 + 2LiBr \quad (3)$$

to react with both aluminum hydride (AlH_3) and aluminum chloride ($AlCl_3$)[2-4] in diethyl ether to produce $Mg(AlH_4)_2$ whereas the third method involved the reaction of $LiAlH_4$ with $MgBr_2$ in diethyl ether.[2,3] The $Mg(AlH_4)_2$ produced was reported to be soluble in diethyl ether and to decompose at 140°; however few experimental details concerning the preparations were given.

Hertwig[5] reported the preparation of $Mg(AlH_4)_2$ by hydrogenolysis of a Grignard reagent in diethyl ether followed by the addition of aluminum chloride to the reaction product. Reactions 4-6 were suggested to describe the course of the reaction. However again few experimental details were given. Hertwig's[5] report seemed reasonable since earlier we had shown[6] that hydrogenolysis of Grignard reagents produces a mixture of MgH_2 and magnesium halide. Therefore, the MgH_2 produced by hydrogenolysis of the Grignard compound in the reaction reported by Hertwig could have reacted with $AlCl_3$ to form $Mg(AlH_4)_2$ in a similar way to that previously reported by Wiberg. The suggested $XMgAlH_4$ could then have arisen from the redistribution of $Mg(AlH_4)_2$ and $MgCl_2$.

$$4RMgX + AlX_3 + 4H_2 \longrightarrow XMgAlH_4 + 3MgX_2 + 4RH \quad (4)$$

$$3RMgX + AlX_3 + 3H_2 \longrightarrow AlH_3 + 3MgX_2 + 3RH \quad (5)$$

$$2XMgAlH_4 \longrightarrow Mg(AlH_4)_2 + MgX_2 \quad (6)$$

Some time ago we had the occasion to prepare $Mg(AlH_4)_2$ by the reaction of $NaAlH_4$ and $MgCl_2$ in dimethyl ether[7] and noticed that the physical properties of this compound were different from the properties reported by Wiberg for $Mg(AlH_4)_2$. The $Mg(AlH_4)_2$ prepared by us was insoluble in diethyl ether and decomposed at 180°.

In 1966 Czech workers[8] verified the preparation of $Mg(AlH_4)_2$ by the reaction of $NaAlH_4$ and $MgCl_2$. Although elemental analysis data were presented, no infrared or X-ray powder diffraction data were given.

It would appear that there is some confusion in the literature concerning the preparation and properties of $Mg(AlH_4)_2$. Since the reaction of a complex metal hydride with MgX_2 in ether solvent to produce $Mg(AlH_4)_2$ is such a fundamental reaction, we decided to study this reaction in detail.

Experimental Section

All operations were carried out either in a nitrogen-filled glove box equipped with a recirculating system to remove oxygen and water[9] or on the bench using typical Schlenk-tube techniques. All glassware was flash flamed and flushed with nitrogen prior to use.

Instrumentation.—Infrared spectra were obtained using a Perkin-Elmer Model 621 high-resolution infrared spectrophotom-

(1) To whom all inquiries should be sent at the Department of Chemistry, Georgia Institute of Technology, Atlanta, Ga. 30332.
(2) E. Wiberg and R. Bauer, *Z. Naturforsch.*, **5b**, 397 (1950).
(3) E. Wiberg, *Angew. Chem.*, **65**, 16 (1953).
(4) E. Wiberg and R. Bauer, *Z. Naturforsch.*, **7b**, 131 (1952).
(5) A. Hertwig, German Patent 921,986 (1955).
(6) W. E. Becker and E. C. Ashby, *J. Org. Chem.*, **29**, 954 (1964).
(7) Ethyl Corp., British Patent 905,985 (1962).
(8) J. Plesek and S. Hermanek, *Collection Czech. Chem. Commun.*, **31**, 3060 (1966).
(9) T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instr.*, **33**, 491 (1962).

Table I

X-Ray Powder Patterns (Main Lines)

Compd	*d*, Å	*I*/*I*$_0$	Compd	*d*, Å	*I*/*I*$_0$
$Mg(AlH_4)_2 \cdot 4THF$	8.70	ms	$IMgAlH_4 \cdot (C_2H_5)_2O$	11.6	s
	7.22	vs		4.58	s
	5.84	m		3.24	ms
	5.50	m		2.83	ms
	4.13	vs			
	3.82	m	$BrMgAlH_4 \cdot (C_2H_5)_2O$	11.6	s
	3.22	m		10.4	m
				8.9	m
$BrMgAlH_4 \cdot 4THF$	11.7	s		4.6	m
	9.71	m			
	8.04	s	$Mg(AlH_4)_2 \cdot 2(C_2H_5)_2O$	10.5	s
	7.11	s		7.9	m
	6.19	m		5.9	s
	4.385	vs		5.6	w
	3.80	m		5.1	w
				4.03	w
$ClMgAlH_4 \cdot 4THF$	11.5	m		3.85	w
	9.4	m		3.05	w, b
	8.0	m		3.50	m
	7.0	m		3.25	w
	6.15	m		2.96	w
	5.69	m		2.90	vw
	5.24	m		2.80	vw
	4.75	m		2.75	w
	4.1	s		2.40	w
				2.18	w

eter. Sodium chloride cells were used. Spectra of solids were obtained in Nujol which had been dried over sodium wire and stored in a drybox. No change was observed in the spectra of either solutions or mulls after standing in the cell for some time. It is therefore concluded that no interaction of the products studied with the cell windows takes place.

X-Ray powder diffraction patterns were run using a Debye–Scherrer camera of 114.6-mm diameter using Cu Kα (1.540 Å) radiation with a nickel filter. Single-walled capillaries of 0.5-mm diameter were used. These were filled in the drybox and sealed with a microburner.

Reagents.—Tetrahydrofuran and benzene (Fisher Certified reagent) were distilled over sodium aluminum hydride immediately before use. Diethyl ether (Fisher Certified reagent) was distilled over lithium aluminum hydride immediately prior to use.

Mercuric halides (Baker Analyzed) were dried under vacuum and used without further purification. Triply sublimed magnesium was obtained from Dow Chemical Co. It was washed with diethyl ether and dried under vacuum prior to use.

Lithium and sodium aluminum hydrides were obtained from Ventron Metal Hydrides Division. Diethyl ether and tetrahydrofuran solutions of these complex metal hydrides were prepared by adding dry, freshly distilled solvent to an appropriate amount of the solid complex metal hydride. The resulting solution was then filtered through a coarse glass fritted filter funnel to which had been added dried Celite filter aid. The resulting clear solutions were standardized by EDTA titration of aluminum.

Preparation of Magnesium Halides in Diethyl Ether and Tetrahydrofuran.[10,11]—In a typical preparation of magnesium halides in ether solvents, 2 g of magnesium was added to 20 g of the appropriate mercuric halide in a 500-ml round-bottom flask with a magnetic stirring bar. Two hundred and fifty milliliters of diethyl ether was then distilled into the flask containing the mixture. The solution was stirred overnight and filtered. The solutions were then standardized by magnesium analysis (EDTA) and halogen analysis (Volhard method). The magnesium to halogen ratio was 1.0:2.00 ± 0.05 in all cases. A qualitative test for residual mercury in the solutions was negative using ferrocyanide and 2,2′-dipyridyl. The solutions were also tested for solvent impurities by hydrolyzing a sample of the solution with distilled water in benzene. The organic matter was then salted out of the water layer into the benzene. The benzene layer was then subjected to analysis by glpc. Only diethyl ether was found to be present in the original solution of MgX_2.

A different method for the preparation of magnesium chloride in diethyl ether had to be used. This was necessary since $MgCl_2$ is insoluble in diethyl ether and it would have been difficult to separate the $MgCl_2$ from the Hg by-product in the previous method. Anhydrous hydrogen chloride in diethyl ether was added to a diethyl ether solution of ethylmagnesium chloride at room temperature in 1:1 molar ratio. The precipitate which was formed was washed with diethyl ether and dried under vacuum. *Anal.* Calcd for $MgCl_2 \cdot (C_2H_5)_2O$: Mg, 14.36; Cl, 41.89. Found: Mg, 14.30; Cl, 41.29.

Analytical Procedures.—Halogen analysis was carried out by the Volhard method. Aluminum analysis was carried out by titration with EDTA. Magnesium analysis was carried out by titration with EDTA. Magnesium analysis in the presence of aluminum was carried out by masking the aluminum with triethanolamine. Lithium analysis was carried out by flame photometry. Hydridic hydrogen analysis was carried out by hydrolyzing a weighed sample of the compound and measuring the volume of gas evolved after passing it through a Dry Ice–acetone trap to remove ether. The amount of ether solvated to a compound was assumed by difference.

General Procedures for Infrared Studies.—A measured amount of magnesium halide in solution was added to a three-neck, 500-ml, round-bottom flask equipped with a three-way stopcock, an addition funnel, and a Dry Ice condenser. The solution of alkali metal aluminum hydride was added in a stepwise fashion in order to establish $MAlH_4$:MgX_2 mole ratios of 0.5:1.0, 1.0:1.0, 1.5:1.0, 2.0:1.0, and 3.0:1.0. After each addition the solution was stirred for 15 min and any precipitate formed was allowed to settle. A sample of the supernatant liquid was taken with a syringe through the three-way stopcock (under strong nitrogen flush) and the infrared cell filled in the drybox. All

(10) B. K. Lewis, *Dissertation Abstr.*, **20**, 2544 (1960).
(11) E. C. Ashby and R. C. Arnott, *J. Organometal. Chem.* (Amsterdam), **14**, 1 (1968).

TABLE II
INFRARED DATA (SOLUTION SPECTRA, cm^{-1})

$Mg(AlH_4)_2 \cdot 4THF$	$BrMgAlH_4 \cdot 4THF$	$LiAlH_4 \cdot (C_2H_5)_2O$
1730 m	1725 s	1740 s
800 w	795 m	755 m
750 m	760 m	
$ClMgAlH_4 \cdot 4THF$	$BrMgAlH_4 \cdot (C_2H_5)_2O$	$LiAlH_4 \cdot THF$
1715 s	1780 s	1691 s
795 m	760 m	760 m
760 m		
		$NaAlH_4 \cdot THF$
		1680 s
		772 m

reactions were carried out such that the resulting concentration of the reaction mixture was between 0.1 and 0.2 *M*.

General Procedure for the Isolation of Intermediates.—The alkali metal aluminum hydride was added to the magnesium halide in a ratio of 1.0:1.0. Any solid formed at this ratio was filtered and analyzed, and its infrared spectrum and X-ray powder pattern were obtained. The resulting solutions were then fractionally crystallized, the separate fractions were analyzed, and their infrared spectra and X-ray powder patterns were obtained.

A. Reactions of $NaAlH_4$ and MgX_2 in Tetrahydrofuran. (1) Reaction of Sodium Aluminum Hydride and Magnesium Chloride in Tetrahydrofuran.—When $NaAlH_4$ was added to $MgCl_2$ in THF in a mole ratio of 0.5:1.0, a precipitate was formed. The infrared spectrum of the solution at this point showed bands at 1715, 795, and 760 cm^{-1}. At a $NaAlH_4$:$MgCl_2$ ratio of 1.0:1.0 the bands at 1715 and 795 cm^{-1} increased in intensity and more precipitate was formed. Elemental analysis and an X-ray powder pattern of this solid showed it to be NaCl. At a $NaAlH_4$:$MgCl_2$ ratio of 1.5:1.0 the intensity of the infrared bands noted above decreased and more precipitate was formed. At a 2.0:1.0 ratio, no infrared bands appeared in the Al–H stretching and deformation regions and more precipitate was formed. At a 3.0:1.0 ratio bands appeared at 1680 and 772 cm^{-1} characteristic of $NaAlH_4$ in tetrahydrofuran. No more precipitate was formed. The solid was filtered and gave an X-ray powder pattern consisting of lines for NaCl and some other substance. This solid was then subjected to Soxhlet extraction with tetrahydrofuran. A white solid was obtained from this extraction which gave lines in the powder pattern which were the same as the lines in the previous pattern with the NaCl lines subtracted (see Table I). The infrared spectrum of this solid showed absorption bands at 1725, 1025, 920, 875, 785, and 740 cm^{-1}. A 77% yield of $Mg(AlH_4)_2 \cdot 4THF$ was obtained. *Anal.* Calcd for $Mg(AlH_4)_2 \cdot 4THF$: Mg, 6.49; Al, 14.41; H, 2.13. Found: Mg, 7.06; Al, 14.90; H, 2.24.

In a separate experiment, $NaAlH_4$ was added to $MgCl_2$ in tetrahydrofuran in a mole ratio of 1.0:1.0. A precipitate formed which was filtered. The resulting filtrate was then subjected to crystallization by solvent removal. The infrared spectrum of this solid in Nujol gave bands at 1730, 1070, 1030, 920, 880, and 745 cm^{-1}. For the major lines in the X-ray powder pattern see Table I. *Anal.* Calcd for $ClMgAlH_4 \cdot 4THF$: Cl, 9.36; Mg, 6.41; Al, 7.12; H, 1.05. Found: Cl, 9.58; Mg, 6.77; Al, 7.22; H, 1.13.

(2) Sodium Aluminum Hydride and Magnesium Bromide in Tetrahydrofuran.—The course of the reaction of $NaAlH_4$ and $MgBr_2$ in tetrahydrofuran was followed by infrared analysis. The results were similar to those reported for the previous system.

In a separate experiment, the solution containing the reaction product of $NaAlH_4$ and $MgBr_2$ in a mole ratio of 1.0:1.0 was treated in the same way as the $ClMgAlH_4$ solution. The infrared spectrum of the solid in Nujol gave absorption bands at 1715, 1070, 1030, 915, 875, 795, and 745 cm^{-1}. The X-ray powder pattern is shown in Table I. *Anal.* Calcd for $BrMgAlH_4 \cdot 4THF$: Br, 28.85; Mg, 5.71; Al, 6.37; H, 0.94. Found: Br, 29.49; Mg, 6.40; Al, 6.91; H, 0.96.

TABLE III
INFRARED DATA (MULL SPECTRA, cm^{-1})

$Mg(AlH_4)_2 \cdot 4THF$	$Mg(AlH_4)_2 \cdot 2THF$	$Mg(AlH_4)_2$
1725 s	1785 s	1855 s
1025 s	1730 s	1830 s
920 w		
875 m		
785 s		
740 s		
$Mg(AlH_4)_2 \cdot 2(C_2H_5)_2O$	$ClMgAlH_4 \cdot 4THF$	$ClMgAlH_4 \cdot 2THF$
1800 s	1730 s	1775 s
1285 w	1070 w	1039 m
1190 w	1030 m	880 m
1150 m	920 w	810 m
1090 m	880 m	745 m
1045 s	745 s	
995 w		$ClMgAlH_4$
895 w		1850 s
740 s		1830 s
$BrMgAlH_4 \cdot 4THF$	$BrMgAlH_4 \cdot (C_2H_5)_2O$	$IMgAlH_4 \cdot (C_2H_5)_2O$
1715 s	1830 s	1800 s
1070 w	1290 w	1285 w
1030 m	1260 w	1190 w
915 w	1190 w	1150 w
875 m	1150 w	1090 m
795 s	1090 m	1050 m
745 s	1040 m	900 m
	1000 w	890 w
	900 w	810 s
	750 s	
	720 s	

(3) Sodium Aluminum Hydride and Magnesium Iodide in Tetrahydrofuran.—At 0.5:1.0 addition of a solution of $NaAlH_4$ in tetrahydrofuran to solid MgI_2 in tetrahydrofuran, the infrared analysis of the filtrate showed an absorption band at 1730 cm^{-1}. At a 1.0:1.0 ratio, a shoulder appeared on the low-frequency side of the absorption band noted above. The intensity of the band at 1730 cm^{-1} was not increased. The X-ray powder pattern of the solid after the 1:1 addition showed it to be a mixture of $MgI_2 \cdot 6THF$ and $Mg(AlH_4)_2 \cdot 4THF$. Further addition of $NaAlH_4$ increased the intensity of the shoulder until at a ratio of 10:1.0 the entire band centered at 1680 cm^{-1}. A yield of 58% for $Mg(AlH_4)_2 \cdot 4THF$ was obtained. The solid at 10:1.0 addition was analyzed. *Anal.* Calcd for $Mg(AlH_4)_2 \cdot 4THF$: Mg, 6.49; Al, 14.41; H, 2.13; I, 0.0. Found: Mg, 7.06; Al, 14.93; H, 2.24; I, 0.0. Infrared and X-ray powder pattern data are given in Tables I–III.

B. Reactions of $LiAlH_4$ and MgX_2 in Tetrahydrofuran. (1) Lithium Aluminum Hydride and Magnesium Chloride in Tetrahydrofuran.—At a 0.5:1.0 ratio of $LiAlH_4$ in tetrahydrofuran to $MgCl_2$ in tetrahydrofuran, infrared analysis of the clear filtrate showed absorption bands at 1715, 795, and 760 cm^{-1}. At a 1.0:1.0 ratio these bands increased in intensity and broadened somewhat. At 1.5:1.0 ratio the bands increased in intensity, and a shoulder appeared at the low-frequency side of the 1715-cm^{-1} band. At a 2.0:1.0 ratio these bands increased in intensity, and at a 3.0:1.0 ratio, what was the shoulder in the previous addition became the main band and was centered around 1691 cm^{-1}. The band at 760 cm^{-1} broadened and its intensity increased to a greater extent than the 795-cm^{-1} band. ($LiAlH_4$ in tetrahydrofuran has infrared absorption bands at 1691 and 763 cm^{-1}.) No precipitate was observed even at 3.0:1.0 addition.

In a separate experiment, $LiAlH_4$ was added to $MgCl_2$ in tetrahydrofuran in 1:1 ratio. The solvent was then removed under vacuum and the infrared spectrum and X-ray powder pattern of the resulting solid were obtained. The solid was shown to be a mixture of LiCl and $ClMgAlH_4 \cdot 4THF$.

(2) Lithium Aluminum Hydride and Magnesium Bromide in Tetrahydrofuran.—Similar results were obtained as in the

previous system. No precipitate was observed even at $LiAlH_4$ to $MgBr_2$ ratios as high as 5.0:1.0.

(3) Lithium Aluminum Hydride and Magnesium Iodide in Tetrahydrofuran.—When $LiAlH_4$ in tetrahydrofuran was added to MgI_2 in tetrahydrofuran, no absorption bands appeared in the infrared spectrum of the solution which were different from those of pure solvent until a $LiAlH_4$:MgI_2 ratio of greater than 2.0:1.0 was attained. At this point absorption bands at 1691 and 760 cm^{-1} appeared indicative of $LiAlH_4$ in solution. The precipitation of solid material in this reaction was obscured by the fact that the MgI_2 reactant is insoluble in THF. The X-ray powder diffraction pattern of the solid product showed the compound to be $Mg(AlH_4)_2 \cdot 4THF$. A yield of 55% for $Mg(AlH_4) \cdot 4THF$ was obtained.

C. Reactions of $NaAlH_4$ and MgX_2 in Diethyl Ether. Sodium Aluminum Hydride and Magnesium Bromide in Diethyl Ether.—Magnesium bromide in diethyl ether was added to $NaAlH_4$ in diethyl ether in a ratio of 1.0:2.0. The solution was stirred for 4 days. At the end of this time no bands in the Al–H stretching and deformation regions were found in the infrared spectrum of the solution. An X-ray powder pattern of the solid showed lines due to NaBr and some other compound which was not $MgBr_2$ or $NaAlH_4$. The infrared spectrum of the solid had bands at 1800, 1285, 1190, 1150, 1090, 1045, 995, 895, and 740 cm^{-1}. The white solid was subjected to Soxhlet extraction. The infrared spectrum of the resulting solid in Nujol exhibited absorption bands at 1800, 1285, 1190, 1150, 1090, 1045, 995, 895, and 740 cm^{-1}. The X-ray powder diffraction pattern is given in Table I. The total yield of $Mg(AlH_4)_2 \cdot 2(C_2H_5)_2O$ was 80%. *Anal.* Calcd for $Mg(AlH_4)_2 \cdot 2C_2H_5O$: Mg, 10.37; Al, 23.03; H, 3.41. Found: Mg, 9.43; Al, 23.96; H, 3.50.

D. Reactions of $LiAlH_4$ and MgX_2 in Diethyl Ether. (1) Lithium Aluminum Hydride and Magnesium Chloride in Diethyl Ether.—Lithium aluminum hydride in diethyl ether was added to $MgCl_2$ in diethyl ether in a mole ratio of 2.0:1.0. The solution was stirred for 2 days. The solid obtained was analyzed. *Anal.* Found: Cl, 50.43; Mg, 2.96; Al, 7.27. The X-ray powder pattern showed only LiCl. The infrared spectrum of the solid gave no definite bands in the Al–H stretching region. After removing some of the solvent from the filtrate a solid was obtained and analyzed. *Anal.* Found: Cl, 16.17; Mg, 12.53; Al, 24.02; Li, 3.15. The X-ray powder pattern gave lines for LiCl and some other compounds. The infrared spectrum of the solid gave bands at 1845, 1780, 1190, 1150, 1090, 1040, 995, and 900 cm^{-1}.

When $LiAlH_4$ was added to $MgCl_2$ in diethyl ether in a mole ratio of 1.0:1.0, the precipitate obtained was analyzed. *Anal.* Found: Cl, 43.91; Mg, 7.25; Al, 11.66; Li, 6.17. The X-ray powder pattern showed lines for LiCl and another compound which did not correspond to the compound in the 2:1 case. The solid obtained by removing the solvent from the filtrate was analyzed. *Anal.* Found: Cl, 22.42; Mg, 12.99; Al, 10.84; Li, 1.27. The X-ray powder pattern gave lines for LiCl. In addition to the lines for LiCl, other lines were observed which corresponded to the second solid in the 2:1 case. The infrared spectrum of this solid gave bands at 1800, 1260, 1195, 1150, 1095, 1045, 1000, and 900 cm^{-1}. The solution spectra of the 2:1 and 1:1 case both gave absorption bands at 1780 cm^{-1} and shoulders on the low-frequency side.

(2) Lithium Aluminum Hydride and Magnesium Bromide in Diethyl Ether.—At a 0.5:1.0 ratio of $LiAlH_4$ to $MgBr_2$ in diethyl ether, absorption bands at 1780 and 760 cm^{-1} appeared in the infrared spectrum of the solution. At a 1.0:1.0 ratio a shoulder on the low-frequency side of the 1780-cm^{-1} band appeared. At a 1.5:1.0 ratio, the bands increased in intensity and the band at 760 cm^{-1} broadened. At a 2.0:1.0 ratio, the bands at 1780 and 1740 cm^{-1} were of equal intensity. At a 3.0:1.0 ratio the bands at 1740 cm^{-1} increased in intensity.

A precipitate was initially formed which gave an indefinite analysis. However, it contained only 2% of the total magnesium.

In a separate experiment, lithium aluminum hydride in diethyl ether was added to $MgBr_2$ in diethyl ether in a mole ratio of 1.0:1.0. The solvent was then removed and a solid was obtained. The X-ray powder pattern showed LiBr but not $LiAlH_4$ or $MgBr_2 \cdot (C_2H_5)_2O$. For the infrared spectrum of the solid in Nujol see Table III. *Anal.* Calcd for LiBr + $BrMgAlH_4 \cdot 2(C_2H_5)_2O$: Li, 1.89; Br, 43.65; Mg, 6.64; Al, 7.37. Found: Li, 1.87; Br, 40.74; Mg, 6.45; Al, 6.45.

(3) Lithium Aluminum Hydride and Magnesium Iodide in Diethyl Ether.—No infrared absorption bands other than diethyl ether appeared up to a $LiAlH_4$:MgI_2 ratio of 1.0:1.0. A white solid was obtained up to this ratio and analyzed. *Anal.* Calcd for $IMgAlH_4 \cdot (C_2H_5)_2O$: I, 49.53; Mg, 9.49; Al, 10.53. Found: I, 49.23; Mg, 9.52; Al, 10.67. Addition of more $LiAlH_4$ gave infrared bands corresponding to $LiAlH_4$. A yield of product was 72%. For the X-ray powder diffraction pattern and infrared spectrum of the solid see Tables I and III.

Reaction of Magnesium Aluminum Hydride and Magnesium Chloride in Tetrahydrofuran.—When equimolar amounts of $Mg(AlH_4)_2$ and $MgCl_2$ in THF were mixed, the resulting solution gave an infrared spectrum corresponding to that of $ClMgAlH_4$. The removal of the solvent gave a solid whose infrared spectrum and X-ray powder pattern were identical with those of $ClMgAlH_4 \cdot 4THF$.

Reaction of Lithium Bromide and Magnesium Aluminum Hydride in Diethyl Ether.—When equimolar amounts of LiBr and $Mg(AlH_4)_2$ were mixed in diethyl ether, the resulting solution exhibited infrared absorption bands at 1780, 1740 (both of equal intensity), 793, and 762 cm^{-1}. See Figure 2.

Results and Discussion

In the present study $LiAlH_4$ and $NaAlH_4$ were allowed to react with $MgCl_2$, $MgBr_2$, and MgI_2 in diethyl ether and tetrahydrofuran. It is important that this reaction was studied in such detail since the course of the reaction is dependent on the nature of the alkali metal, the halide, the solvent, and the solubility of the alkaki metal halide by-product. The discussion will be divided roughly into two parts (eq 7), namely, those combinations of reactants that produce $Mg(AlH_4)_2$ as the reaction product and those combinations of reactants that either stop at the $XMgAlH_4$ stage or produce an equilibrium mixture of products.

$$MAlH_4 + MgX_2 \longrightarrow MX + XMgAlH_4 \xrightarrow{MAlH_4} MX + Mg(AlH_4)_2 \quad (7)$$

When $NaAlH_4$ was allowed to react with $MgCl_2$ in tetrahydrofuran in a mole ratio of 1.0:1.0, a white precipitate appeared which was shown by elemental and X-ray powder pattern analyses to be NaCl. The infrared spectrum of the reaction solution showed bands at 1715, 795, and 760 cm^{-1}. None of these bands corresponds to $NaAlH_4$ but they are characteristic of the Al–H stretching and deformation regions. When this solution was subjected to fractional crystallization, successive fractions gave elemental analyses corresponding to the empirical formula $ClMgAlH_4 \cdot 4THF$. The X-ray powder pattern of this solid shows no lines due to $MgCl_2 \cdot 2THF$, $Mg(AlH_4)_2 \cdot 4THF$, $NaAlH_4$, or NaCl. Furthermore, the infrared spectrum of this solid shows bands at 1730, 1070, 1030, 920, 880, and 745 cm^{-1} which are not characteristic of either $MgCl_2$ or $Mg(AlH_4)_2 \cdot 4THF$. Also no bands characteristic of Mg–H were observed. It would appear then that the product produced in this reaction is $ClMgAlH_4 \cdot 4THF$ and not a physical mixture of $MgCl_2$ and $Mg(AlH_4)_2$ or $MgCl_2$, MgH_2, and AlH_3.

As one adds more $NaAlH_4$ to the $MgCl_2$ in tetrahydrofuran until the mole ratio is 2.0:1.0, more precipitate is formed and the infrared spectrum of the solution shows no bands in the Al–H or Mg–H stretching and deformation regions. The infrared spectrum of this solid in Nujol shows bands at 1725, 1025, 920, 875, 785, and 740 cm^{-1}. The X-ray powder pattern of the solid showed NaCl in admixture with some other compound. The elemental analysis of the solid was consistent with a mixture of NaCl and $Mg(AlH_4)_2 \cdot 4THF$. Soxhlet extraction of this solid with tetrahydrofuran yielded crystals which produced an analysis consistent with $Mg(AlH_4)_2 \cdot 4THF$. The infrared spectrum of the solid-extracted product was the same as the original product mixture and the X-ray powder pattern showed all the lines of the mixture after subtracting out the lines due to NaCl. The infrared and powder pattern data of the extracted solid were not consistent with the description of the product as a physical mixture of MgH_2 and AlH_3. Thus it appears clear that the reaction of $NaAlH_4$ and $MgCl_2$ in tetrahydrofuran proceeds stepwise to produce first the soluble $ClMgAlH_4$ and then the insoluble $Mg(AlH_4)_2$

$$NaAlH_4 + MgCl_2 \xrightarrow{THF} ClMgAlH_4 + NaCl \quad (8)$$

$$ClMgAlH_4 + NaAlH_4 \xrightarrow{THF} Mg(AlH_4)_2 + NaCl \quad (9)$$

When $MgCl_2$ in tetrahydrofuran was added to $Mg(AlH_4)_2 \cdot 4THF$, the insoluble $Mg(AlH_4)_2$ dissolved. The resultant solution produced an infrared spectrum identical with that exhibited by $ClMgAlH_4$. Fractional crystallization of the solution yielded solid fractions whose X-ray powder patterns and infrared analyses were consistent with those of $ClMgAlH_4 \cdot 4THF$ prepared from $NaAlH_4$ and $MgCl_2$ in 1:1 stoichiometry

$$MgCl_2 + Mg(AlH_4)_2 \xrightarrow{THF} 2ClMgAlH_4 \quad (10)$$

Since the reaction of $NaAlH_4$ with $MgCl_2$ in tetrahydrofuran is a stepwise reaction to produce $ClMgAlH_4$ and then $Mg(AlH_4)_2$, any $Mg(AlH_4)_2$ formed in the initial stages of the reaction would rapidly redistribute with $MgCl_2$ to form $ClMgAlH_4$. The $Mg(AlH_4)_2$ formed in these reactions was insoluble in tetrahydrofuran, diethyl ether, and the common nonpro ic organic solvents contrary to the earlier reports by W berg.[2-4]

When $NaAlH_4$ was allowed to react with $MgBr_2$ in THF, results similar to the reactions with $MgCl_2$ were observed; *i.e.*, at a 1:1 ratio $BrMgAlH_4$ was formed and at a 2:1 ratio $Mg(AlH_4)_2$ was formed. Since odium bromide is also insoluble in tetrahydrofuran, $Mg(AlH_4)_2$ produced in this reaction contains 2 molar equiv of NaBr.

Magnesium aluminum hydride could be prepared essentially halogen free by allowing $NaAlH_4$ and MgI_2 to react in tetrahydrofuran at a mole ratio of 10:1.0. Since the NaI by-product is soluble in THF, $Mg(AlH_4)_2$ precipitates from solution halogen free. Attempts to prepare $IMgAlH_4$ in THF were unsuccessful owing to the disproportionation of this compound to MgI_2 and $Mg(AlH_4)_2$ in tetrahydrofuran. Since both MgI_2 and $Mg(AlH_4)_2$ are insoluble in THF, elemental analysis indicates an empirical formula $IMgAlH_4$. However infrared and powder diffraction analyses show that this solid is a physical mixture of MgI_2 and $Mg(AlH_4)_2$ (eq 11). This disproportionation was demonstrated

$$NaAlH_4 + MgI_2 \xrightarrow{THF} NaI + [IMgAlH_4] \longrightarrow 0.5MgI_2\downarrow + 0.5Mg(AlH_4)_2\downarrow \quad (11)$$

further by adding $IMgAlH_4 \cdot (C_2H_5)_2O$ to tetrahydrofuran (eq 12). The reaction was very exothermic and

$$2IMgAlH_4 + (C_2H_5)_2O \xrightarrow{THF} MgI_2 \cdot 6THF\downarrow + Mg(AlH_4)_2 \cdot 4THF\downarrow + (C_2H_5)_2O \quad (12)$$

the resultant solid produced an infrared spectrum and X-ray powder pattern consistent with those of a mixture of $MgI \cdot 6THF$ and $Mg(AlH_4)_2 \cdot 4THF$.

A second reaction which produces $Mg(AlH_4)_2$ essentially halogen free is that between $LiAlH_4$ and MgI_2 in tetrahydrofuran at a mole ratio of 3:1 or 4:1. Here again the disproportionation of $IMgAlH_4$ to MgI_2 and $Mg(AlH_4)_2$ prevents the isolation of $IMgAlH_4$ in THF. The solubility of the LiI by-product enables the $Mg(AlH_4)_2$ to be obtained halogen free

$$2LiAlH_4 + MgI_2 \xrightarrow{THF} Mg(AlH_4)_2 + 2LiI \quad (13)$$

When $NaAlH_4$ was allowed to react with $MgBr_2$ in diethyl ether at a mole ratio of 2.0:1.0, a white precipitate formed. This solid was shown by X-ray powder diffraction and infrared data to be a mixture of NaBr and $Mg(AlH_4)_2$ (eq 14). Thus it is possible to prepare

$$2NaAlH_4 + MgBr_2 \xrightarrow{(C_2H_5)_2O} Mg(AlH_4)_2 + 2NaBr \quad (14)$$

$Mg(AlH_4)_2$ in both tetrahydrofuran and diethyl ether using the specific combination of reagents described.

The reactions described until now have been reasonably straightforward. When the alkali metal aluminum hydrides were added to the MgX_2 in 1:1 stoichiometry, $XMgAlH_4$ was formed. Upon addition of more $MAlH_4$, the $XMgAlH_4$ reacted further to form $Mg(AlH_4)_2$. In most of these cases the insolubility of the alkali metal halide by-product or of the MgI_2 seems to play an important role. If now we concentrate on the reactions where the alkali metal halide by-product is soluble, we see that the reaction proceeds in a somewhat different fashion.

When $LiAlH_4$ was allowed to react with $MgCl_2$ in tetrahydrofuran in a 1.0:1.0 ratio, the reaction filtrate exhibited infrared absorption bands corresponding to $ClMgAlH_4$ as was observed in the reaction of $MgCl_2$ with $NaAlH_4$ in tetrahydrofuran. No precipitate formed in the reaction since LiCl is soluble in tetrahydrofuran. When the 1.0:1.0 ratio of reactants was exceeded, the bands due to $ClMgAlH_4$ did not decrease in intensity as in the previous cases. Instead as more $LiAlH_4$ was added, bands due to the $LiAlH_4$ increased in intensity. Thus, instead of $Mg(AlH_4)_2$ being produced, an equilibrium resulted as shown in eq 15.

$$LiAlH_4 + MgCl_2 \overset{THF}{\rightleftharpoons} ClMgAlH_4 + LiCl \quad (15)$$

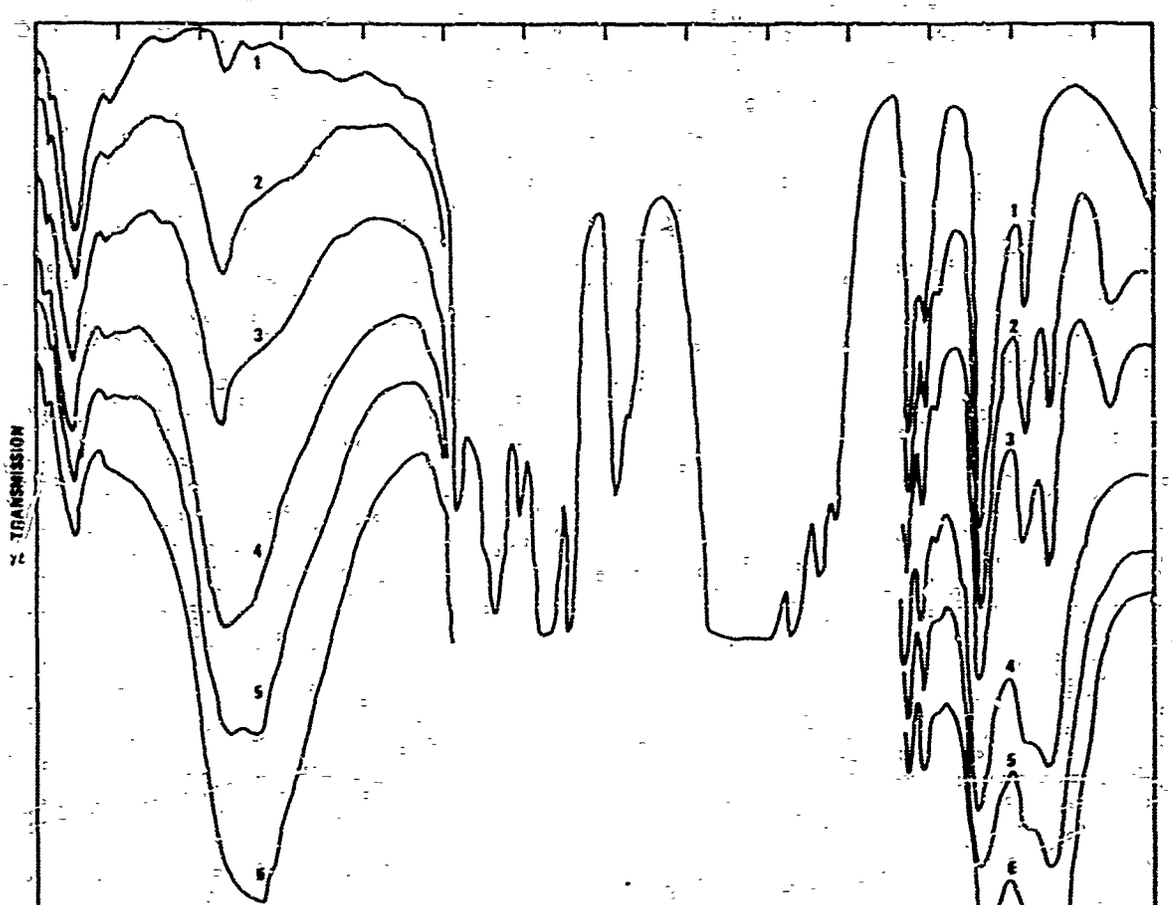

Figure 1.—Reaction of $LiAlH_4$ and $MgBr_2$ in diethyl ether. Ratio of $LiAlH_4$:$MgBr_2$: (1) $(C_2H_5)_2O$, (2) 0.5:1.0, (3) 1.0:1.0, (4) 1.5:1.0, (5) 2.0:1.0, (6) 3.0:1.0.

In order to determine if $ClMgAlH_4$ was the actual intermediate being formed, $LiAlH_4$ was added to $MgCl_2$ in tetrahydrofuran in a 1:1 ratio. The solution was then fractionally crystallized and the resulting solids were subjected to X-ray, infrared, and elemental analyses. All of the analyses showed that $ClMgAlH_4$·4THF and LiCl were the major products present.

Similar results were obtained when $LiAlH_4$ and $MgBr_2$ were allowed to react in tetrahydrofuran (eq 16). The products of this reaction are $BrMgAlH_4$·4THF and LiBr. Here no solid was formed in the reaction even when the $LiAlH_4$:$MgBr_2$ ratio was 5.0:1.0, once again indicating the lack of formation of $Mg(AlH_4)_2$ (insoluble in tetrahydrofuran). Lithium bromide is soluble in tetrahydrofuran.

$$LiAlH_4 + MgBr_2 \overset{THF}{\rightleftharpoons} BrMgAlH_4 + LiBr \qquad (16)$$

The reaction of $LiAlH_4$ and $MgBr_2$ in diethyl ether, previously reported by Wiberg to form $Mg(AlH_4)_2$, also showed this equilibrium behavior. The equilibrium in diethyl ether may not lie as far to the right as in tetrahydrofuran (eq 16) since the $LiAlH_4$ appears in the solution spectrum sooner than in tetrahydrofuran. A small amount of initial precipitate was formed; however it was found to contain less than 2% of the total magnesium in the reaction. No additional precipitate was formed even at an $LiAlH_4$:$MgBr_2$ ratio of 3:1. The equilibrium nature of the reaction of $LiAlH_4$ and $MgBr_2$ in diethyl ether was verified by the infrared examination of the reaction solution as the $LiAlH_4$ was added to the $MgBr_2$. Figure 1 shows that even at an $LiAlH_4$:$MgBr_2$ ratio of 0.5:1.0, unreacted $LiAlH_4$ is present in the reaction mixture. The Al–H stretching band (1740 cm^{-1}) and the Al–H deformation band (755 cm^{-1}) characteristic of $LiAlH_4$ in diethyl ether increases as the $LiAlH_4$:$MgBr_2$ ratio increases. At the $LiAlH_4$:$MgBr_2$ ratio of 2:1 it is clear that the spectrum represents a mixture of $BrMgAlH_4$ and $LiAlH_4$ in approximately equimolar quantities rather than $Mg(AlH_4)_2$ reported by Wiberg (compare the spectrum for $Mg(AlH_4)_2$·$2(C_2H_5)_2O$ in Figure 2).

In order to test the equilibrium hypothesis an ether solution of LiBr was added to $Mg(AlH_4)_2$ obtained by the reaction of $NaAlH_4$ and $MgBr_2$ in diethyl ether. The resulting solution (eq 17) produced absorption

$$LiBr + Mg(AlH_4)_2 \xrightarrow{(C_2H_5)_2O} BrMgAlH_4 + LiAlH_4 \qquad (17)$$

bands of equal intensity at 1780 and 1740 cm^{-1}. $LiAlH_4$ in diethyl ether has an absorption band at 1740 cm^{-1} and $BrMgAlH_4$ has an absorption band at 1780

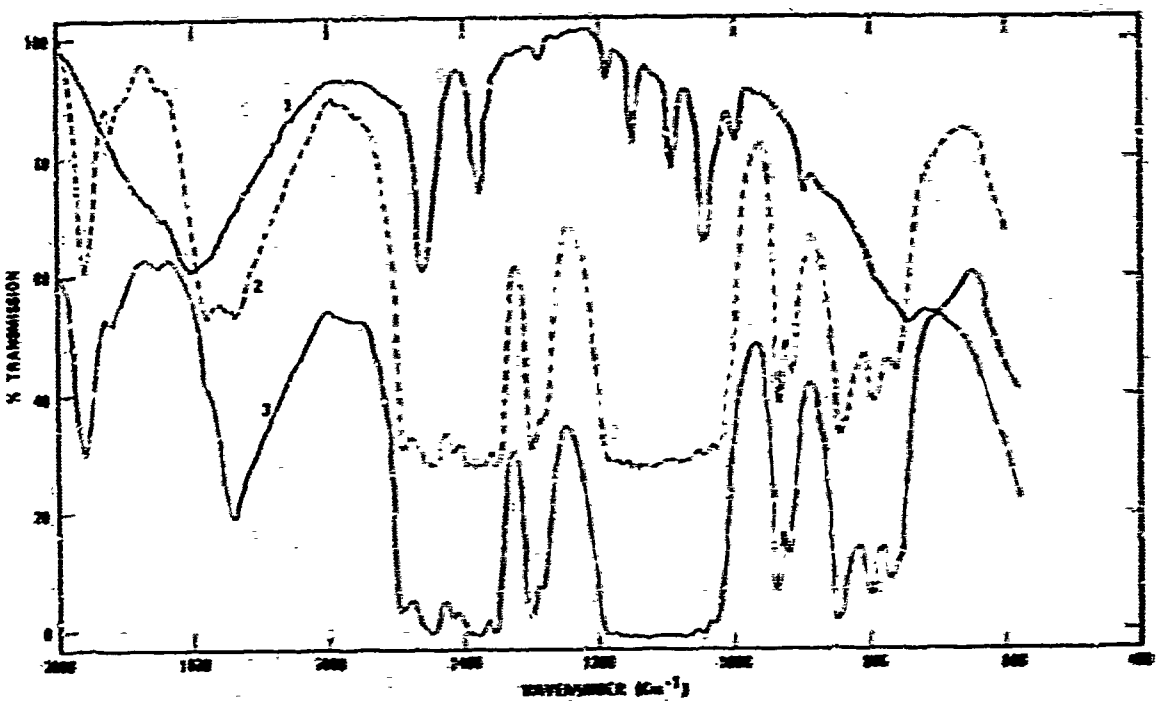

Figure 2.— $Mg(AlH_4)_2 \cdot 2(C_2H_5)_2O$ in Nujol; (2) $Mg(AlH_4)_2 + LiBr \xrightarrow{(C_2H_5)_2O} LiAlH_4 + BrMgAlH_4$; (3) $LiAlH_4$ in $(C_2H_5)_2O$.

cm^{-1} in diethyl ether.) The infrared spectrum (Figure 2) was consistent with that expected for a mixture of $LiAlH_4$ and $BrMgAlH_4$. The spectrum was also identical with the solution spectrum of the 2.0:1.0 addition product of $LiAlH_4$ to $MgBr_2$ (eq 18).

$$2LiAlH_4 + MgBr_2 \overset{(C_2H_5)_2O}{\rightleftharpoons} BrMgAlH_4 + LiBr + LiAlH_4 \quad (18)$$

In diethyl ether the reaction of $LiAlH_4$ with MgI_2 (eq 19) was found to proceed in a similar fashion to the reaction of $LiAlH_4$ and $MgBr_2$. At a stoichiometry of 1:1, a white solid was obtained which was shown by infrared, X-ray powder diffraction, and elemental analyses to be $IMgAlH_4 \cdot (C_2H_5)_2O$. Further addition of $LiAlH_4$ did not produce $Mg(AlH_4)_2$.

$$LiAlH_4 + MgI_2 \xrightarrow{(C_2H_5)_2O} IMgAlH_4 + LiI \quad (19)$$

The results of the reaction of $LiAlH_4$ and $MgCl_2$ in diethyl ether are somewhat confusing. There is evidence that both $ClMgAlH_4$ and $Mg(AlH_4)_2$ are formed. Both the 1:1 and 2:1 reaction mixtures appear to contain $ClMgAlH_4$. In the 2:1 case there is evidence also that some $Mg(AlH_4)_2$ is formed.

Infrared studies in the solid state of the compounds prepared indicate that the degree of covalent bonding between the magnesium and the tetrahydridoaluminate group is dependent upon the degree of solvation. This is especially true in the case of the tetrahydrofuran solvates. Both $Mg(AlH_4)_2$ and $ClMgAlH_4$ are obtained from tetrahydrofuran solution as the tetrakis(tetrahydrofuranates). The four tetrahydrofuran solvate molecules probably exist in a tetrahedral arrangement about the magnesium atom. This would increase the size of the cation thereby stabilizing the molecule. The solid-state infrared spectra of $Mg(AlH_4)_2 \cdot THF$ and $ClMgAlH_4 \cdot THF$ both exhibit single sharp bands (25-50 cm^{-1} half-width) at 1725 and 1730 cm^{-1}, respectively. Since the bands are not split, the four hydrogens on the AlH_4 group must be equivalent with no bridging. This would be consistent with an ionic model.

On the other hand, when two of the tetrahydrofuran solvate molecules are removed from the tetrakis solvate, the infrared spectrum of the resulting solid shows that the Al-H stretching band has moved to a higher frequency and split into two bands at 1755 and 1730 cm^{-1}. This indicates that the compound has become more covalent and that there are probably bridging hydrogens as indicated by the two bands. If $Mg(AlH_4)_2$ is completely desolvated, the Al-H stretching frequency shifts to an even higher frequency and remains split with bands at 1855 and 1830 cm^{-1}.

When $ClMgAlH_4 \cdot 4THF$ is dissolved in benzene and recrystallized, the solid obtained contains only two THF solvate molecules. The infrared spectrum of this solid shows that the Al-H stretching band has shifted to a higher frequency. However, the band is not split, although it is somewhat broad and is centered at 1775 cm^{-1}. Upon complete desolvation the Al-H stretching band again shifts to a higher frequency and this time splits into two bands: 1850 and 1830 cm^{-1}.

These data indicate that upon desolvation $Mg(AlH_4)_2$ and $ClMgAlH_4$ exhibit more covalent character through bridging hydrogens. Lithium aluminum hydride in the solid state, which is considered to be covalent, has two bands in the solid-state infrared spectrum at 1770 and 1625 cm^{-1}.

Summary

In summary, the reactions of complex metal hydrides with magnesium halides in ether solvents can be

divided into two classes. The first class includes those reactions which produce an insoluble alkali metal halide by-product. These reactions produce at a 1:1 $MAlH_4 + MgX_2$ stoichiometry an isolatable $XMgAlH_4$ compound and upon addition of more $MAlH_4$ produce $Mg(AlH_4)_2$ in good yield. An exception to this is the MgI_2 case in THF. Here the "$IMgAlH_4$" disproportionates to MgI_2 and $Mg(AlH_4)_2$ immediately so that "$IMgAlH_4$" cannot be isolated from tetrahydrofuran solution. The second class includes those reactions where the alkali metal by-product is soluble. Here an equilibrium is produced according to

$$MAlH_4 + MgX_2 \rightleftharpoons XMgAlH_4 + MX \qquad (20)$$

Magnesium aluminum hydride is not formed even when $MAlH_4$ is added in excess.

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13. ABSTRACT

For the second contract year work ~~has been~~ carried out to prepare new and unusual simple and complex metal hydrides of the main group metals, lithium, beryllium, magnesium, boron and aluminum. The philosophy of this endeavor is to pursue both the understanding of fundamental chemical reactions in the hydride area that are poorly understood or incorrectly reported as well as directing major attention to the synthesis of new compounds. By the pursuit of understanding as well as synthesis it is hoped that entirely new concepts will be uncovered which will lead to major contributions. The most notable contributions of the present report are the synthesis of the first alkali metal magnesium hydrides ($KMgH_3$, $NaMg_2H_5$), the first stable $HMgX$ compounds ($HMgNR_2$), the development of extremely economic routes to aminoalanes [$HAl(NR_2)_2$] and aminoboranes [$HB(NR_2)_2$], first synthesis of $RMgH$ compounds, the completion of detailed mechanistic studies of several fundamental reactions in the hydride area, and the inauguration of DTA-TGA investigations of both simple and complex metal hydrides.

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